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# SOME STUDIES ON THE BEHAVIOR OF W-RE THERMOCOUPLE MATERIALS AT HIGH TEMPERATURES

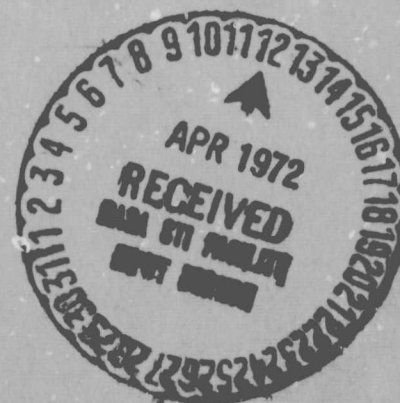
by

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

INTERAGENCY AGREEMENT  
NASA ORDER NO. C-61545-B



U. S. DEPARTMENT OF COMMERCE  
National Bureau of Standards  
INSTITUTE FOR BASIC STANDARDS  
Washington, D. C. 20234

N72-20401

Unclass  
23070

CSCL 14B G3/14

(CATEGORY)

(NASA CR OR TMX OR AD NUMBER)

FACIL

(NASA-CR-72884) SOME STUDIES ON THE  
BEHAVIOR OF W-RE THERMOCOUPLE MATERIALS AT  
HIGH TEMPERATURES G.W. Burns, et al  
(National Bureau of Standards) Feb. 1972

47 p

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1. Report No. NASA CR-72884		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle SOME STUDIES ON THE BEHAVIOR OF W-Re THERMOCOUPLE MATERIALS AT HIGH TEMPERATURES				5. Report Date February, 1972	
				6. Performing Organization Code	
7. Author(s) G. W. Burns and W. S. Hurst				8. Performing Organization Report No. 2210414-2	
9. Performing Organization Name and Address U. S. Department of Commerce National Bureau of Standards Institute for Basic Standards Washington, D. C. 20234				10. Work Unit No.	
				11. Contract or Grant No. C-61545-B	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				13. Type of Report and Period Covered Contractor Report	
				14. Sponsoring Agency Code	
15. Supplementary Notes Project Manager, I. Warshawsky, Chief, Instrument Research Division, National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, and G. E. Glawe, Technical Consultant.					
16. Abstract  Bare 0.25 mm diameter W-Re alloy thermoelements (W, W-3% Re, W-5% Re and W-25% Re) and BeO-insulated W-3% Re and W-25% Re thermoelements have been examined for metallurgical, chemical and thermal emf changes after testing for periods up to 1000 hours at temperatures principally in the range 2000 to 2400 K. Environments for the tests consisted of high purity argon, hydrogen, helium or nitrogen gases. Commercially obtained bare-wire thermoelements typically exhibited a shift in their emf-temperature relationship upon initial exposure. The shift was completed by thermally aging the W-3% Re thermoelement for 1 hour and the W-25% Re thermoelement for 2 minutes at 2400 K in argon or hydrogen. Aged thermoelements experienced no appreciable drift with subsequent exposure at 2400 K in the gaseous environments. The chemically "doped" W-3% Re thermoelement retained a small-grained structure for exposure in excess of 50 hours at 2400 K. BeO-insulated thermoelement assemblies showed varied behavior that depended upon the method of exposure. However, when the assemblies were heated in a furnace, no serious material incompatibility problems were found if the materials were given prior thermal treatments. Thermocouples, assembled from aged W-3% Re and W-25% Re thermoelements and degassed sintered BeO insulators, exhibited a drift of only 2 to 3 K during exposure in argon at 2070 K for 1029 hours.					
17. Key Words (Suggested by Author(s)) Tungsten-Rhenium Alloys Beryllium Oxide Thermal Emf-Temperature Relationship Thermocouples Drift Microstructure			18. Distribution Statement  Unclassified - Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 42	
				22. Price* \$3.00	

\* For sale by the National Technical Information Service, Springfield, Virginia 22151

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# SOME STUDIES ON THE BEHAVIOR OF W-RE THERMOCOUPLE MATERIALS AT HIGH TEMPERATURES

by G.W. Burns and W.S. Hurst

National Bureau of Standards  
Temperature Section

## SUMMARY

This report describes an investigation of the effect of exposure at 2400 K of bare-wire (0.25 mm diameter) W-Re alloy thermoelements, and the effect of exposure at 2000 and 2073 K of W-3% Re and W-25% Re thermoelements insulated with sintered BeO tubing. Exposure periods up to 1000 hours were employed. Environments for the tests consisted of high purity argon, helium, nitrogen, and hydrogen gases at a pressure of about  $1 \times 10^5 \text{ N}\cdot\text{m}^{-2}$  (1 atm).<sup>1</sup> Short term tests (< 50 hours) in argon and hydrogen with bare-wire thermoelements were also performed at exposure temperatures varying from 1200 to 3000 K. Changes in the thermoelectric properties of the thermoelements were determined either during or after the high temperature exposure. Material characterization included conventional metallographic examination and chemical analyses, both before and after high temperature exposure.

Bare-wire thermoelements were exposed to high temperatures by heating the thermoelements electrically within a stainless steel test chamber in the presence of high purity gaseous atmospheres. The changes in the emf-temperature relationship of the thermoelements after exposure were determined by intercomparing the exposed thermoelements with previously unheated thermoelements from the same wire lots. For these intercomparisons, the thermoelements were heated in argon in a high temperature calibration furnace.

The changes in thermal emf and in metallurgical structure of bare-wire W-3% Re and W-25% Re thermoelements that occurred with exposure at 2400 K in  $\text{N}_2$  or He environments were similar to that found in earlier tests in argon (ref. 1). After an initial shift in the thermal emf, which occurred within the first 50 hours of exposure, no further significant change (drift) was detected for exposure periods up to 1000 hours. For the W-3% Re thermoelement, the initial shift depended slightly on the environmental gas that was used.

Thermal aging studies were performed in argon and hydrogen environments with the W-3% Re and W-25% Re thermoelements to determine the time-temperature parameters necessary to complete the initial shift in emf. Thermal aging was complete in the W-3% Re thermoelement after exposure for 1 hour at 2400 K. For the W-25% Re thermoelement, thermal aging was complete after exposure for 1 hour at 2000 K or for 2 minutes at 2400 K. With thermal aging according to these schedules, the microstructure of both thermoelements remains small grained, and the materials possess sufficient room temperature ductility for subsequent thermocouple assembly.

The thermoelectric behavior of other W-Re alloy thermoelements (chemically "doped" W and W-5% Re, and "undoped" W-5% Re) after exposure at 2400 K in argon was similar to that observed for "doped" W-3% Re and "undoped" W-25% Re thermoelements in earlier investigations (ref. 1). However, in contrast to the "doped" W-3% Re thermoelement, where the microstructure remained small grained after exposure in argon for periods up to 1000 hours, the "doped" W and W-5% Re thermoelements exhibited a large-grained structure (secondary recrystallization) after exposure for periods in excess of 50 hours.

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<sup>1</sup> 1 atm =  $1.01325 \times 10^5 \text{ N}\cdot\text{m}^{-2}$ .

W-3% Re and W-25% Re thermoelements were assembled in high purity sintered BeO insulating tubing and then exposed in argon at nominally 2000 K. Two different experimental methods for exposure were used. In one method, the insulated thermoelements were exposed to high temperature by heating of the thermoelement electrically. Exposure was in the environmental test chambers used previously in the bare-wire studies. After exposure, changes in the emf-temperature relationship of the thermoelements were determined in the same manner that was used to determine changes in bare-wire thermoelements. The other method employed an ultra-high-vacuum, high temperature furnace, which was back-filled with high purity argon gas for the tests. Compatibility tests of single thermoelements with BeO were performed by suspending the insulated thermoelement directly in the furnace hot-zone. Tests of BeO-insulated W-3% Re versus W-25% Re thermocouples, where measurements of the thermal emf were made during the exposure, were performed with thermocouples inserted into a Ta blackbody enclosure that was suspended in the furnace hot-zone.

Exposure of the BeO-insulated thermoelements in argon at 2000 K gave results which varied according to the method of thermal exposure. W-3% Re and W-25% Re thermoelements, which were heated electrically for 50 hours, experienced a preferential loss of W. In the W-25% Re thermoelements the preferential loss of W was quite large in some instances, but it was confined to a surface layer and resulted in only a moderate change in thermal emf. (Thermocouples comprised of thermoelements exposed in this manner exhibited a change equivalent to less than 10 K at 2073 K.) BeO-insulated thermoelements exposed for 50 hours in the furnace exhibited no observable evidence of W loss if the BeO was first sufficiently degassed. W-3% Re versus W-25% Re thermocouples, fabricated from thermally aged thermoelements and insulated with well degassed sintered BeO tubing, exhibited a drift of only 2 to 3 K during exposure in argon at 2073 K for 1029 hours. Significant reductions in the impurity levels of sintered BeO insulating tubing were found after degassing and (particularly) after exposure for 1029 hours at 2073 K in argon while in the presence of tantalum.

## INTRODUCTION

This report describes a continuing study of the component materials for ceramic-insulated, metal-sheathed, W-Re type thermocouple sensors. The studies are directed towards establishing some of the parameters which are important in design and construction of thermocouple sensors, where reliable operation for thousands of hours at temperatures above 1800 K is required.

Previous studies, performed under NASA Order No. C-30968-B, focused on the behavior of the bare (non-insulated) thermoelements (ref. 1). In these studies, 0.25 mm diameter W-3% Re and W-25% Re thermoelements were exposed at temperatures of 2200 to 2600 K in environments of high purity hydrogen or argon (nominally 1 atm pressure) or in high vacuum of less than  $1.3 \times 10^{-6}$  N·m<sup>-2</sup> ( $1 \times 10^{-8}$  torr)<sup>2</sup> for periods up to 1000 hours. With exposure of the thermoelements at these temperatures, the changes in the emf-temperature relationship<sup>3</sup> that occurred could be conveniently classified in two ways: Initial short-term (up to 50 hours) changes were designated as a "shift", and subsequent long-term changes were designated as a "drift". In the argon and hydrogen environments, the thermoelements exhibited a positive shift in their emf-temperature relationship with initial exposure at 2400 K. After this initial shift, further exposure in argon or hydrogen at 2400 K for periods up to 1000 hours

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<sup>2</sup> 1 torr =  $1.01325 \times 10^5 / 760$  N·m<sup>-2</sup>. All values of pressure are indicated equivalent nitrogen pressures.

<sup>3</sup>The change in the emf-temperature relationship of a thermoelement is defined as the emf-temperature relationship of a thermocouple that is comprised of that thermoelement versus an unheated "as received" thermoelement from the same spool (lot) of wire, when the reference junctions are maintained at 273.15 K and the unheated "as received" thermoelement is designated as the negative leg of the thermocouple.

resulted in no significant drift in the emf-temperature relationship of the thermoelements. W-3% Re and W-25% Re thermoelements from three different matched lots of wire were examined in the previous studies. Exposure at 2400 K for 1 hour was found to be sufficient to complete the initial shift in the thermal emf. The magnitude of the initial shift varied with the lot of wire. For W-3% Re thermoelements from a given lot of wire<sup>4</sup>, the magnitude of the shift varied slightly with the environment; the shift after exposure in hydrogen averaged slightly less (about 120  $\mu$ V at 2073 K) than the shift after exposure in argon. For W-25% Re thermoelements from a given lot of wire, the shift was the same in both environments. For a given matched lot of wire, the positive initial shift for the W-3% Re thermoelement exceeded that for the W-25% Re thermoelement, and hence the thermocouple pair also exhibited an initial positive shift. For the three matched lots examined, the initial shifts after exposure in argon were equivalent to about +2, +6 and +18 K at 2073 K.

In the previous study, bare W-3% Re and W-25% Re thermoelements that were exposed in high vacuum ( $< 1 \times 10^{-8}$  torr) at temperatures above 2200 K exhibited a continual drift in their emf-temperature relationship as a result of preferential evaporation of Re. The drift was strongly dependent upon the temperature of exposure. The drift (at 2073 K) for the thermocouple pair was about -180 K after 500 hours of exposure at 2400 K. A drift of about the same magnitude occurred after only 50 hours of exposure at 2600 K, while the drift after 500 hours at 2200 K was negligible ( $< 5$  K).

The present work involves continuing studies on the behavior of the bare thermoelements. Annealing studies were undertaken in order to develop suitable time-temperature parameters for aging of the thermoelements. Parameters for aging were sought which would minimize the initial shift in the thermal emf and yet leave the thermoelements with sufficient room temperature ductility to permit subsequent fabrication of thermocouple sensors. The previous studies with W-3% Re and W-25% Re thermoelements were extended to include investigations of their behavior in gaseous helium and nitrogen environments. The studies were also extended to include other commercially available W-Re alloy thermoelements.

In addition, studies were initiated to examine the behavior of thermoelements and thermocouples when insulated with high purity sintered BeO tubing. These included investigations of the chemical compatibility of the W-Re alloys with BeO in high purity gaseous argon and an investigation of the thermoelectric stability of BeO-insulated W-3% Re versus W-25% Re thermocouples during exposure in argon at 2073 K for periods up to 1000 hours.

In this report, the general terms shift and drift are also used to characterize the changes in the emf-temperature relationship of thermoelements and thermocouples that result from exposure to high temperatures. As in the previous report, the time interval during which the shift occurs is referred to as the thermal aging period. Tests with insulated thermoelements and thermocouples in gaseous argon employed thermoelements that first were thermally aged in argon to remove the effect of the initial shift.

## EXPERIMENTAL APPARATUS AND PROCEDURES

### STUDIES OF BARE(NON-INSULATED) THERMOELEMENTS

The experimental apparatus and procedures for exposure of the bare thermoelements were described previously (ref. 1). Briefly, the apparatus consists of bakeable stainless steel test chambers in which 90 to 100 cm long thermoelements can be exposed to high temperatures in high purity gaseous environments (1 atm) or in high vacuum ( $< 1 \times 10^{-8}$  torr). During high temperature exposure, the thermoelements are heated electrically with alternating current (60 Hz) and their temperature is determined and monitored with a calibrated visual optical pyrometer. Corrections are applied to account for the transmittance of the glass

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<sup>4</sup>Only one lot was tested in both argon and hydrogen at 2400 K; for thermoelements from this lot the shift in the emf-temperature relationship at 2073 K averaged about +380  $\mu$ V in argon and +260  $\mu$ V in hydrogen.

window on the test chamber and the spectral emissivity of the test wires (ref. 2). After exposure for specified periods of time, the thermoelements are removed from the test chamber and measurements are made of their thermal emf versus an unheated "as received" thermoelement from the same spool (lot) of wire. The measurements are typically made at 200 K intervals from 673 to 2073 K<sup>5</sup> by heating the samples in argon in a resistance heated calibration furnace.

This procedure gives the relative changes<sup>6</sup> in the thermal emf-temperature relationship of the thermoelement due to exposure. The maximum uncertainty in the measurement of relative changes is estimated not to exceed  $\pm 30 \mu\text{V}$  at 1273 K and  $\pm 50 \mu\text{V}$  at 2073 K for all the lots of wire tested in the present studies. The uncertainty in the measurements results primarily from the thermoelectric non-uniformity of the particular lot of wire tested. The change in the thermal emf-temperature relationship of a thermocouple pair, in which both thermoelements have been exposed, may be obtained by combining algebraically the changes measured for the separately exposed thermoelements. For the thermocouple pair, the maximum uncertainty in the value of the change is assumed to be twice the uncertainty given above for the thermoelement.

Following the convention of the previous report, the change in the thermal emf of the exposed thermoelements and thermocouples at a given temperature is expressed in terms of an equivalent temperature change ( $\Delta T$ ) in the following manner: For the thermocouples,  $\Delta T$  is obtained by dividing the change in the thermal emf of the thermocouples at a given temperature by the thermoelectric power<sup>7</sup> ( $dE/dT$ ) at the same temperature;  $\Delta T$  for the separate thermoelements is obtained similarly, except that for the W-25% Re thermoelement (negative element of the thermocouples), a negative value of the thermoelectric power of the thermocouples<sup>8</sup> is used, so that a positive change in emf results in a negative  $\Delta T$ . In this manner, changes occurring in the separate thermoelements are expressed in terms of their individual effects upon the thermocouples, and the algebraic sum of the  $\Delta T$ 's for each of the thermoelements equals the  $\Delta T$  for the thermocouple.

#### STUDIES WITH BeO-INSULATED THERMOELEMENTS AND THERMOCOUPLES

Preliminary studies. A series of preliminary tests were conducted to examine the chemical and physical behavior of BeO-insulated W-3% Re and W-25% Re thermoelements after exposure in argon (1 atm) at 2000 K for periods of 50 hours. These preliminary tests were performed in the same apparatus that was used for exposing bare (non-insulated) thermoelements. 5 to 15 cm lengths of sintered double-bore BeO insulating tubing were strung onto the test thermoelement by inserting the thermoelement through only one bore of the tubing. The insulated thermoelement was then hung from two electrodes in the test chamber so that the entire length between the electrodes (effective heated portion) was covered by BeO tubing. For exposure, the thermoelement was heated electrically with alternating current (60 Hz) and its temperature was ascertained from measurements of its electrical resistance. The resistance per unit length as a function of temperature for bare thermoelements from the same lots of wire was determined from prior measurements, which used a visual optical pyrometer to determine the temperature with appropriate corrections to account for the spectral emissivity of the thermoelements. After exposure in argon at 2000 K for 50 hours, the change in the emf-temperature relationship of the test thermoelement was determined following the procedure described in the previous section for bare thermoelements.

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<sup>5</sup>Values of temperature in this report are given on the International Practical Temperature Scale of 1968 (IPTS-68).

<sup>6</sup>A positive value for the relative change in the emf of an exposed thermoelement at a given temperature signifies that the thermoelement is thermoelectrically positive with respect to an unheated "as received" thermoelement from the same spool (lot) of wire; that is, the emf of the exposed thermoelement has increased at that temperature.

<sup>7</sup>The values of thermoelectric power for the W versus W-25% Re, W-3% Re versus W-25% Re and W-5% Re versus W-25% Re thermocouples at 2073 K are about 18, 16, and 14  $\mu\text{V/K}$ , respectively.

<sup>8</sup>The values of  $\Delta T$  presented in this report for the W-25% Re thermoelement are calculated by using the thermoelectric power of the W-3% Re versus W-25% Re thermocouple.

In these preliminary tests, the BeO tubing was usually given a high temperature vacuum degas prior to placement on the test thermoelement. The degassing was performed in the test chamber by heating the BeO tubing within a helical heating element formed from 0.5 mm diameter W-3% Re wire. The heating element was about 0.5 cm in diameter by 15 cm long. The degassing schedule varied, but typically the heating element temperature was increased in about 200 K steps to temperatures as high as 2100 K over a period of 20 to 30 hours; the pressure was maintained at less than  $5 \times 10^{-7}$  torr. The thermoelements were degassed by heating electrically for 1 hour at about 1570 K at a pressure of less than  $5 \times 10^{-6}$  torr. They were then aged in argon at 2400 K for a time period sufficient to complete the initial shift in thermal emf. Prior to testing, the insulated thermoelement assemblies were usually given a low temperature degas (to about 1000 K) by heating for several hours in a vacuum of less than  $5 \times 10^{-7}$  torr. For most tests, the assemblies were fabricated in air but for a few tests the assembly of the degassed components was performed in an inert gas.

The method of exposure employed in these preliminary tests has several serious limitations. First, axial and radial temperature gradients exist in the insulated thermoelement during a test due to the manner in which it is heated, and only an average value for the temperature of the thermoelement is obtained by measuring its resistance. Chemical and physical changes that occur in the thermoelements during a test act to alter their resistance and therefore to increase the error in the determination of the average temperature. Resistance changes of the order of 10% were not uncommon during these tests and for this reason it is estimated that the average temperature of the thermoelement was not known to better than  $\pm 150$  K in a typical test. Under the experimental conditions, a determination of the average temperature of the thermoelement from observations of the brightness temperature of the BeO with an optical pyrometer was subject to errors that were probably as large as this. This resulted primarily because the spectral emissivity (ref. 3) of the BeO tubing and the radial temperature gradient through it were not known with sufficient accuracy.

Studies in the high temperature furnace. An ultra-high-vacuum, high temperature furnace was put into operation midway through the program and this furnace was used for vacuum degassing of materials, additional BeO-W-Re wire compatibility studies in argon, and for evaluating the long-time (1000 hours) performance of BeO-insulated W-3% Re versus W-25% Re thermocouples in argon. The furnace incorporates in its design many of the features of present day vacuum technology. All-metal and metal-to-ceramic construction is utilized throughout, and all components are capable of sustaining repeated and extended bakeouts at 525 K without damage or loss of vacuum integrity. A high-speed, ultra-high vacuum pumping system is employed, and facilitates rapid attainment of ultra-clean environments. Some of the principal features of this furnace are illustrated in Fig. 1. The furnace has a tungsten wire-mesh heating element 6.4 cm in diameter by 30.5 cm long oriented with its central axis vertical. The heating element is surrounded by tungsten radiation shields that are enclosed within a water-cooled copper coldwall. The coldwall assembly is mounted within a stainless steel vacuum chamber, which is also water cooled.

The portion of the copper coldwall and radiation shields directly above the heating element is removable through a 10 cm diameter port at the top of vacuum chamber, thus providing complete access to the interior of the heating element for installing materials and experimental devices for test. An optical path is provided through the wire-mesh heating element, side radiation shields, and copper coldwall for viewing the interior of the heating element through a 3.8 cm diameter viewing port on the side of the vacuum chamber. A Corning type 7056 glass window is mounted on the viewing port. A stainless steel shutter is provided within the vacuum chamber that fully covers the view port when closed and does not obscure any part of the port when open. Electrical connections between the heating element and a power transformer are made through two water cooled, metal-ceramic sealed electrodes that extend into the chamber through ports on the vacuum chamber. The electrodes also serve to support the wire-mesh heating element and maintain its electrical isolation from the tungsten shields and copper coldwall.

A sorption pump roughing system and a high-speed, ultra-high vacuum pumping system are used for evacuating the vacuum chamber. The roughing system, consisting of three molecular sieve type sorption pumps mounted on a stainless steel manifold, is connected to the vacuum chamber through a bakeable metal-sealed valve. The high-speed, high-vacuum pumping system consists of a 400 liter/s sputter ion pump and an accessory (three filament cartridge type) titanium sublimation pump (TSP).

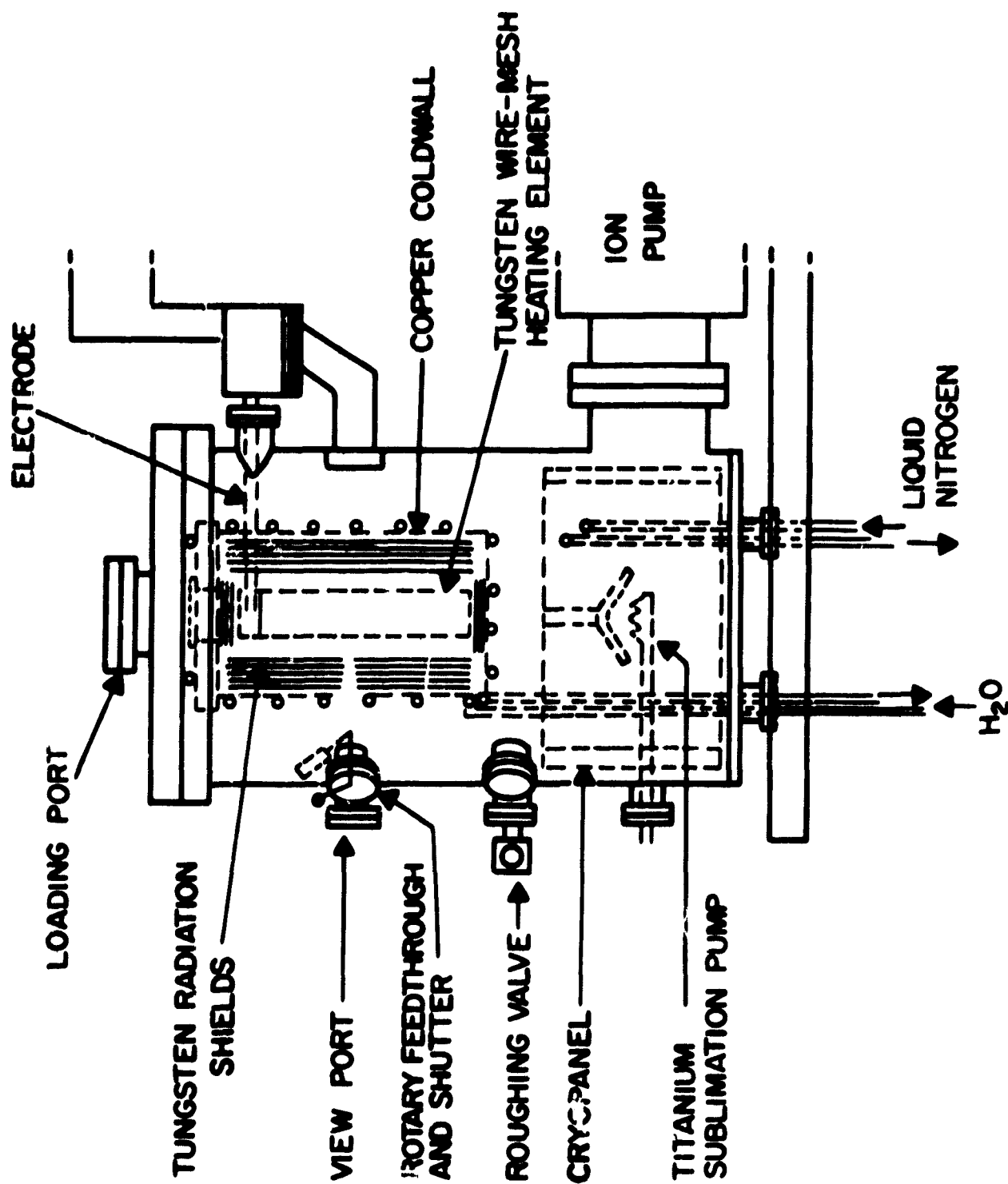


Figure 1. Principal features of the ultra-high-vacuum, high temperature furnace. The roughing system, water cooling of stainless steel vacuum chamber, bakeout heaters and shroud, gas manifold, and ionization gauge are not shown.

A cylindrical stainless steel shroud (cryopanel), cooled with liquid nitrogen, surrounds the TSP and enhances pumping. An optically-dense baffle is installed above the TSP and shields the upper chamber region from titanium deposition. The pressure within the chamber is measured with a nude Bayard-Alpert type ionization gauge. For bakeout, ceramic-insulated metal clad heaters are attached to the exterior walls of the vacuum chamber and ion pump; these systems are surrounded by an aluminum bakeout shroud. Bakeout heater power controls are interlocked electrically with pressure and temperature sensing controls so as to permit unattended (automatic) bakeout of the chamber and ion pump at 525 K. If, after evacuating and baking the system, a gaseous environment is desired, high purity gas from a cylinder of compressed gas may be introduced through a stainless steel manifold that is connected to the vacuum chamber by an all-metal ballable valve.

Power to the wire-mesh heating element is supplied through a 67 kVA Silicon Controlled Rectifier (SCR) type proportional power controller and a 47 kVA air-cooled stepdown transformer. The temperature within the hot-zone is controlled by the indirect method of controlling the power supplied to the mesh heating element. For automatically controlling the power at the desired level (set point), a closed loop control system is provided. The closed loop control utilizes a thermal watt converter type power sensor in conjunction with a high-response electronic controller to feed back an appropriate control signal to the SCR proportional power controller. The electronic controller incorporates an adjustable set point, which allows the power level to be selected with a resolution of better than 0.1%. The controller has a 20 millisecond response and includes features such as adjustable gain, rate and reset time controls. At maximum gain settings, the control system has a sensitivity equivalent to about 2 watts. The power controls are electrically interlocked with other controls and automatically shut off the heating element power if the cooling water flow drops below a safe operating level, or if the pressure in the vacuum chamber rises above an adjustable preset value.

With the furnace at ambient temperature (no power to the furnace), pressures of less than  $5 \times 10^{-11}$  torr<sup>9</sup> have been achieved within 10 hours after a 10 hour bakeout of the chamber and the pumping system at about 525 K. The furnace is designed to produce hot-zone temperatures up to 3000 K while maintaining the pressure in the  $10^{-8}$  torr range; with the furnace chamber filled with a high purity inert gas or with hydrogen gas at a pressure of 1 atmosphere, it is designed to produce hot-zone temperatures in excess of 2700 K.

At elevated temperatures, the temperature in the hot-zone of the furnace responds very rapidly to changes in heating element power. Hence, precise automatic control of the power provides a reasonably sensitive and reproducible method for controlling the hot-zone temperature. With the furnace chamber filled with 1 atmosphere pressure of argon, a temperature stability over a period of 1000 hours of  $\pm 4$  K at 2073 K has been achieved. Over a 24 hour period, the temperature stability has been typically within  $\pm 2$  K at 2073 K, and for shorter periods (20 to 30 minutes),  $\pm 0.5$  K.

For vacuum degassing and processing of sintered BeO tubing, the tubing was supported in the hot-zone of the furnace with a W-Re wire basket, which was formed by interweaving 0.125 and 0.25 mm diameter wires. Additional studies of the chemical and physical behavior of W-3% Re and W-25% Re thermoelements when heated within sintered BeO insulating tubing were performed in 1 atmosphere pressure of high purity argon ( $< 10$  ppmv total impurities) at 2000 K. For these studies, the W-3% Re and W-25% Re thermoelements were inserted into the BeO insulating tubing and then the insulated thermoelements were suspended from the hot shield assembly for exposure in the hot-zone of the furnace.

For evaluation of the long-time (1000 hours) performance of BeO-insulated W-3% Re versus W-25% Re thermocouples in argon at 2073 K, the tantalum blackbody enclosure shown in Fig. 2 was suspended in the hot-zone of the furnace. This design closely approximates an ideal blackbody if the walls of the enclosure are at a uniform temperature. Using calculations derived by DeVos (ref. 4), it is estimated that the effective emittance of this blackbody enclosure is greater than 0.997. The BeO-insulated thermocouples for test were inserted through the tantalum supporting tube so that their measuring junctions were within the blackbody enclosure. The thermocouple wires were led out of the furnace chamber through metal-glass feedthroughs at the top of the chamber, and the wire exits were sealed

<sup>9</sup>Indicated equivalent nitrogen pressure.

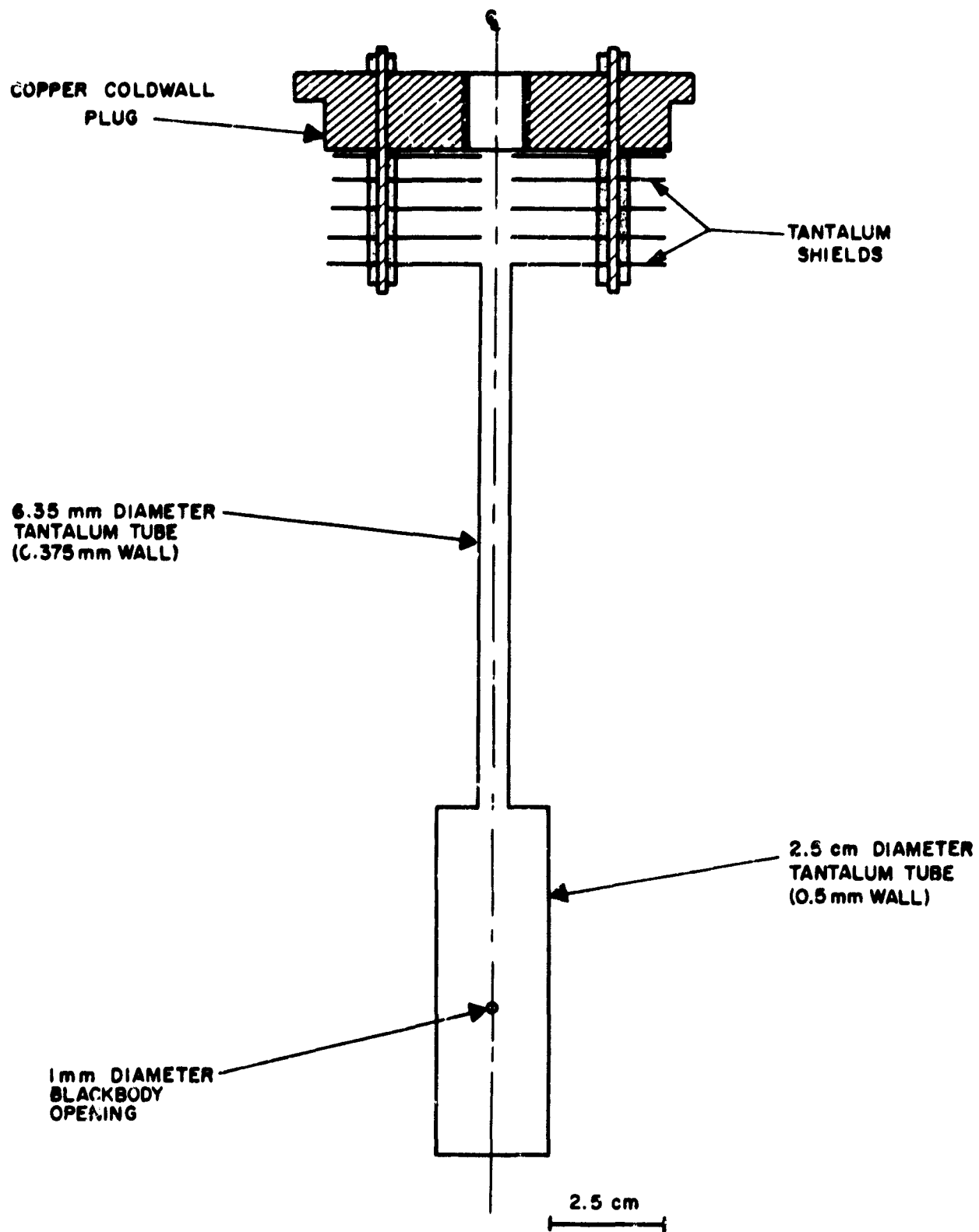


Figure 2. Tantalum blackbody enclosure for the high temperature furnace.

2 with a solvent-free epoxy resin. The metal-glass feedthroughs were mounted on a 15 cm o.d. ultra-high vacuum flange that sealed to a mating flange on the 10 cm diameter loading port of the furnace. The reference junctions of the thermocouples were maintained at 273.15 K in an ice bath. During a test, the temperature of the tantalum blackbody enclosure was determined with a visual optical pyrometer, and also with an automatic photoelectric optical pyrometer. The pyrometers used were of commercial design and were calibrated<sup>10</sup> by relating the pyrometer lamp current to the brightness or blackbody temperature. In use, the pyrometer lamp current was determined by measuring the voltage drop across a 1 ohm standard resistor in series with the lamp. All voltage measurements, including the emfs of test thermocouples, were made with a precision potentiometer having a limit of error of less than  $\pm$  (0.015% of voltage measured +2  $\mu$ V).

The temperature of the blackbody and the thermal emf of the thermocouples were measured about every 20 to 30 hours during the long term test. For measurements with the visual optical pyrometer, a set of four brightness matches was taken by each of two observers. For each brightness match the pyrometer lamp current was measured and the emf of each thermocouple was also measured. The four readings of the pyrometer lamp current for each observer were averaged, as were the four corresponding values of emf measured for each thermocouple. From the average value of pyrometer lamp current a value of temperature was computed. A small correction was applied to account for the transmittance of the furnace window. A similar procedure of averaging was followed for measurements with the automatic photoelectric pyrometer. Hence, three bases of reference were provided for such tests: visual optical pyrometer with observer No. 1; visual optical pyrometer with observer No. 2; and the automatic photoelectric pyrometer.

#### MATERIALS TESTED

Thermocouple materials for the studies were taken from "matched lots"<sup>11</sup> of: (A) unalloyed tungsten and W-25% Re thermoelements; (B) W-3% Re and W-25% Re thermoelements; and (C) W-5% Re and W-25% Re thermoelements. These materials were obtained from two leading commercial suppliers of W-Re type thermocouple wire. All lots were nominally 0.25 mm diameter wire. Of these materials, three types were chemically "doped" by adding small amounts of potassium, silicon and aluminum compounds to the tungsten oxide prior to its reduction to metal. The residual doping elements which remain after the wire forming process modify the changes in metallurgical structure that occur when the wire is exposed to elevated temperatures and result in improvements in the mechanical properties (refs. 5 and 6). The doped materials are the W, the W-3% Re and one class of W-5% Re thermoelements. The other class of W-5% Re and the W-25% Re thermoelements are undoped.

In addition to the matched lots of wire obtained from the commercial thermocouple wire suppliers, a lot of 0.25 mm diameter W-3% Re wire was obtained directly from a major wire manufacturer especially for use in the aging studies. This lot of wire was cleaned and straightened by the manufacturer after being drawn, but was not given a stress-relief anneal. A lot of 0.25 mm diameter W-25% Re wire was also obtained directly from a manufacturer for similar purposes. The manufacturer of this wire reported that, after drawing,

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<sup>10</sup>Calibration was performed by the Optical Radiation Section at NBS.

<sup>11</sup>A "matched lot" of thermoelements is one in which the positive and negative thermoelements have been selected by the supplier so that the emf-temperature relationship of the thermocouple complies to a table within specified limits. One supplier designates the negative thermoelement as W-26% Re when matched with the unalloyed W or the W-5% Re thermoelement, and designates the negative thermoelement as W-25% Re when matched with the W-3% Re thermoelement. All Re concentrations are nominal values only. We have chosen to designate the negative thermoelement of the three types of thermocouples as W-25% Re in this report as a matter of convenience.

it was subjected to a temperature of about 1200 K for a short period (< 1 minute) during a cleaning and straightening process. In contrast, the matched lots of wire acquired from the thermocouple wire suppliers were heat treated to reduce the effects of the mechanical working received during the wire manufacturing processes.

Some lots of the W-3% Re and W-25% Re thermoelements were given a special surface cleaning treatment by the supplier in order to more thoroughly remove surface contaminants introduced during the wire manufacturing process. The cleaning treatment included ultrasonic degreasing, abrading and electro-etching. These materials were used in all of the insulated thermoelement tests as well as in the tests of bare-wire thermoelements in  $N_2$  and He environments.

As part of the characterization of the "as received" materials, the thermal emf of representative thermocouples from each of the matched lots of wire was measured at 200 K increments from 673 to 2073 K. The thermocouples were tested by comparison with W-3% Re versus W-25% Re thermocouples that were from a lot of previously calibrated wire. The measurements confirmed that the emf-temperature relationship of the "as received" thermocouples from each matched lot (as determined with increasing temperature) complied with the suppliers corresponding calibration table (refs. 7 and 8) to within the equivalent of  $\pm 1\%$  of the temperature.

Typical mass spectrographic analyses of representative samples from various wire lots are given in Table 1. Of the dopants reportedly used in the "doped" alloys, only potassium was detected in appreciably larger amounts than in the undoped alloys.

For tests with BeO-insulated thermoelements and thermocouples, high purity sintered double-bore BeO tubing with 0.3 mm diameter bores, 1.1 mm outer diameter and 0.125 mm  $\pm$  0.025 mm web size (space between bores) was used. All tubing was from the same batch which was supplied by the manufacturer in random lengths between 10 and 25 cm long. Quantitative spectrochemical analysis<sup>12</sup> of representative "as received" samples from the batch of tubing indicated their purity to be in excess of 99.8%. The major impurities detected were C (230 ppmw), Al (200 ppmw), Si (120 ppmw), and Mg (90 ppmw), while the total detectable impurities were less than 800 ppmw (a more complete analysis is given in the results section). The manufacturer reported that the tubing was about 97% of the maximum theoretical density. No independent determinations of the density were performed.

Each of the argon, hydrogen, helium and nitrogen gases used in the experiments were an ultra-high purity grade of commercially available compressed gas. The helium gas was certified by the supplier to contain less than 10 ppmv total impurities<sup>13</sup>, and within detectable limits, this was supported by analysis at NBS. The nitrogen gas was certified by the supplier to contain less than 30 ppmv total impurities, and an analysis at NBS indicated that it contained less than 0.1 ppmv hydrocarbons, less than 5 ppmv  $H_2O$ , and less than 1 ppmv  $O_2$ . Typical analyses for the argon and hydrogen gases were reported previously (ref. 1).

Seamless tantalum tubing was used in the construction of the blackbody enclosure (see Fig. 2) for the ultra-high-vacuum furnace. Before use, the blackbody enclosure was given a high temperature vacuum degas. The pressure was maintained at less than  $1 \times 10^{-6}$  torr during the 24 hour degassing cycle, and temperatures up to 2370 K were employed. A mass spectrographic analysis of the Ta components after degassing is given in Table 2. The major impurities detected in the Ta components were W, Nb, K and Cl. The large concentration of W (300 ppmw) might be due in part to some pick-up of W from the furnace heating element during the vacuum degassing process. However, this was not confirmed since samples of the Ta components in the "as received" condition were not analyzed.

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<sup>12</sup>Carbon gas determined by combustion-gas chromatography.

<sup>13</sup>Assumes the gas to be free of neon. In this report ppmv and ppmw denote parts per million by volume and parts per million by weight, respectively.

TABLE I. TYPICAL MASS SPECTROGRAPHIC ANALYSES OF THE W-Re THERMOELEMENTS

(ppmw)

Element	<u>Thermoelement</u>				
	"doped" W	"doped" W-3% Re	"doped" W-5% Re	"undoped" W-5% Re	W-25% Re
Li	0.002	0.004	0.04	0.004	0.004
Be	<0.004	<0.002	0.004	0.03	<0.004
B	0.01	0.02	0.01	0.02	0.02
F	0.4	0.4	1.	0.2	<0.3
Na	10.	20.	20.	10.	20.
Mg	1.	1.	3.	1.	1.
Al	6.	3.	10.	6.	4.
Si	10.	10.	20.	10.	3.
P	0.1	0.2	1.	2.	20.
S	<1.	<3.	0.4	6.	1.
Cl	1.	2.	0.6	1.	3.
K	200.	100.	300.	20.	10.
Ca	2.	10.	2.	2.	4.
Sc	<0.1	<0.1	<0.1	<0.1	<0.1
Ti	2.	<4.	<4.	<4.	<10.
V	0.1	1.	1.	0.2	1.
Cr	10.	3.	10.	10.	10.
Mn	0.02	0.1	0.2	0.2	2.
Fe	50.	50.	100.	30.	50.
Co	0.2	0.1	2.	0.4	0.1
Ni	30.	1.	20.	5.	20.
Cu	0.6	1.	1.	2.	2.
Zn	<0.1	<0.1	<0.1	<0.1	<0.1
Ga	<0.1	<0.1	<0.03	<0.1	<0.1
Ge	1.	2.	2.	2.	10.
As	<0.05	<0.05	<0.02	0.1	<0.5
Se	<0.2	<0.2	<0.2	<0.2	<0.2
Br	0.4	1.	0.5	0.4	0.5
Rb	<0.07	0.1	<0.02	0.2	0.3
Sr	<0.05	0.1	<0.05	0.2	0.2
Y	0.04	0.1	<0.05	<0.1	0.2
Zr	<1.	<10.	<3.	<1.	<20.
Nb (a)	-	-	-	-	-
Mo	5.	100.	20.	10.	100.
Ru	<0.2	<0.2	<0.2	<0.2	<0.2
Rh	<0.06	<0.06	<0.06	<0.06	<0.06
Pd	<0.2	<0.2	<0.4	<0.4	<0.4

(a) Interference from tungsten.

TABLE I, Continued

(ppmw)

Element	Thermoelement				
	"doped" W	"doped" W-3% Re	"doped" W-5% Re	"undoped" W-5% Re	W-25% Re
Ag	≤0.1	≤0.2	≤0.1	≤0.3	≤0.3
Cd	<0.2	<0.1	<0.06	<0.2	<0.1
In	<3.	<6.	<2.	<3.	<6.
Sn	<0.2	<0.1	<0.1	<0.2	0.2
Sb	<0.2	<0.06	<0.06	<0.2	3.
Te	<0.2	<0.2	<0.07	<0.2	<0.2
I	<0.1	<0.06	<0.02	<0.1	<0.03
Cs	<0.1	<0.2	<0.2	<0.5	<0.2
Ba	≤0.1	<0.1	≤0.1	≤0.3	<0.1
La	<3.	<3.	<1.	<3.	<1.
Ce	≤0.1	≤0.4	≤0.2	≤0.3	≤1.
Pr	<0.04	<0.04	<0.04	<0.04	0.1
Nd	<2.	<2.	<1.	<2.	<1.
Sm	<0.1	<0.1	<0.1	<0.1	<0.1
Eu	<0.05	<0.05	<0.05	<0.05	<0.05
Gd	<0.3	<0.3	<0.3	<0.3	<0.3
Tb	<0.3	<0.2	<0.2	<1.	<0.2
Dy	<0.3	<0.2	<0.1	<0.3	<0.2
Ho	<0.03	<0.06	<0.03	<0.03	<0.03
Er	<0.1	<0.2	<0.1	<0.1	<0.1
Tm	<0.03	<0.03	<0.03	<0.03	<0.03
Yb	<0.3	<0.2	<0.1	<0.3	<0.1
Lu	<0.03	<0.03	<0.03	<0.03	<0.03
Hf	<0.1	<0.1	<0.1	<0.1	<0.1
Ta	4.	4.	4.	4.	20.
Re	2.	High	High	High	High
Os	<0.1	<0.1	<0.3	<0.1	<0.3
Ir	<0.05	<0.1	<0.2	<0.05	<0.2
Pt	<3.	<6.	<6.	<6.	<6.
Au	<3.	<3.	<2.	<3.	<2.
Hg	<4.	<10.	<6.	<10.	<6.
Tl	<0.05	<0.1	<0.06	<0.1	<0.1
Pb	0.1	<0.4	<0.2	0.2	≤0.2
Bi	<0.05	<0.2	<0.1	≤0.1	≤0.1
Th	<0.1	0.3	1.	2.	0.4
U	<0.06	<0.06	<0.06	<0.06	<0.06

TABLE II. TYPICAL MASS SPECTROGRAPHIC ANALYSIS OF THE TANTALUM TUBING USED IN CONSTRUCTION OF THE BLACKBODY ENCLOSURE\*

(ppmw)

Element	2.5 cm Diam. Tube	6.35 mm Diam. Tube	Element	2.5 cm Diam. Tube	6.35 mm Diam. Tube
Li	0.04	0.1	Ag (a)	<200.	<70
Be	<0.005	<0.005	Cd	<0.4	<0.4
B	<0.01	<0.01	In	<0.4	<0.4
F	<1.	<1.	Sn	2.	<2.
Na	4.	7.	Sb	<0.3	<0.2
Mg	<0.2	<0.2	Te	<0.7	<0.7
Al	0.07	0.2	I (a)	<20.	<10.
Si	0.7	2.	Cs	<0.3	<0.1
P	0.2	<0.2	Ba	<0.3	<0.3
S	3.	20.	La	<0.2	<0.2
Cl	40.	15.	Ce	<0.04	<0.04
K	40.	40.	Pr	<0.3	<0.1
Ca	7.	15.	Nd	<0.2	<0.2
Sc	<0.07	<0.07	Sm	<0.3	<0.1
Ti	0.1	0.7	Eu	<0.2	<0.05
V	0.06	10.	Gd	<0.5	<0.5
Cr	1.	1.	Tb	<0.3	<0.3
Mn	0.2	0.2	Dy	<0.2	<0.2
Fe	3.	15.	Ho	<0.05	<0.05
Co	<0.1	<0.1	Er	<0.1	<0.1
Ni	<1.	<1.	Tm	<0.03	<0.03
Cu	0.7	0.7	Yb	<1.	<0.5
Zn	<0.4	<0.2	Lu	<0.2	<0.07
Ga	<0.2	<0.2	Hf	<0.4	<0.4
Ge	<0.4	<0.4	W	300.	300.
As	<0.2	<0.2	Re	<0.2	2.
Se	<1.	<0.5	Os	<0.2	<0.2
Br (a)	<400.	<150.	Ir	<0.2	<0.2
Rb	<0.2	<0.07	Pt	<7.	<7.
Sr	<0.05	<0.05	Au	<2.	<2.
Y	<0.03	<0.03	Hg	<0.2	<0.3
Zr	<1.	<1.	Tl	<0.1	<0.3
Nb	200.	20.	Pb	≤1.	≤1.
Mo	2.	5.	Bi	<0.4	<0.4
Ru	<0.2	<0.2	Th	<0.2	<0.2
Rh	<0.2	<0.2	U	<0.05	<0.05
Pd	<0.6	<0.6			

(a) Poor detectability due to memory from previous samples.

\*Blackbody enclosure shown in Fig. 2.

## EXPERIMENTAL RESULTS AND DISCUSSION

### TESTS WITH BARE-WIRE THERMOELEMENTS

Thermoelectric behavior in nitrogen and helium environments. Studies were conducted to determine the thermoelectric changes of bare-wire W-3% Re and W-25% Re thermoelements due to exposure at 2400 K in high purity environments of nitrogen and helium. The thermoelectric behavior observed in both nitrogen and helium was similar to that reported previously for exposure in high purity environments of argon and hydrogen.

The results for W-3% Re thermoelements taken from one lot (spool) of wire and exposed in nitrogen are shown in Fig. 3. The thermoelements experienced an initial positive shift in the emf-temperature relationship during the first 50 hours of exposure. Like the previous results in argon and hydrogen, the shift in thermal emf of the W-3% Re thermoelements is roughly linear with respect to temperature; at 2073 K, it is equivalent to about 6 K. Most of the shift occurs during the first hour of exposure. The slight additional shift that is shown between the 1 and 50 hour exposure periods is smaller than the estimated measurement uncertainty. For exposure periods in excess of 50 hours at 2400 K in nitrogen, the W-3% Re thermoelements exhibited no further significant change (drift) in the emf-temperature relationship. The width of the cross-hatched curve indicates the range of values obtained for thermoelements exposed for 50, 100, 150, 250, 500, 750 and 1000 hours. The range of the values at 2073 K is about 35  $\mu$ V (equivalent to about 2.2 K).

The results for W-25% Re thermoelements taken from one lot (spool) of wire and exposed in nitrogen at 2400 K are shown in Fig. 4. For thermoelements from this particular lot of wire, there is no appreciable initial shift in the emf-temperature relationship, nor is there any significant drift for exposure periods up to 550 hours. The data for thermoelements exposed for periods of 1, 50, 100, 150, 250, 500 and 550 hours are all within the cross-hatched area. The range of the values at 2073 K is about 40  $\mu$ V (equivalent to about 2.5 K).

W-3% Re and W-25% Re thermoelements from these same lots exposed at 2400 K in helium exhibited an initial shift that averaged about the same as for the thermoelements exposed in nitrogen. The long-term behavior of the thermoelements in both the nitrogen and helium environments is illustrated in Fig. 5, where the change in the thermal emf of the thermoelements at 2073 K is plotted against exposure time at 2400 K. In each case, the subsequent drift is insignificantly small (less than 5 K during the exposure times shown).

Thermoelectric behavior in argon and hydrogen environments. W-3% Re and W-25% Re thermoelements from the above lots were also exposed in argon and hydrogen environments at 2400 K. Table III summarizes the changes at 2073 K in the emf-temperature relationship of the W-3% Re thermoelements after exposure in the various environments at 2400 K for 1 and 50 hours. The difference between the shifts in the hydrogen and argon environments after 50 hours exposure is considered measurably significant. Three different lots of W-3% Re thermoelements have been exposed at 2400 K to both the argon and hydrogen environments in this study thus far. Whereas each lot exhibited a different initial shift, the difference between the shift in argon and the shift in hydrogen was about the same for all three lots, and was equal to the equivalent of  $6 \pm 2$  K at 2073 K. For the W-25% Re thermoelements, no significant variation of the shift between different environments (A, H<sub>2</sub>, N<sub>2</sub> or He) was found.

TABLE III. AVERAGE SHIFT IN THE THERMAL EMF-TEMPERATURE RELATIONSHIP AT 2073 K FOR W-3% Re THERMOELEMENTS FROM THE SAME LOT AFTER EXPOSURE AT 2400 K IN VARIOUS GASEOUS ENVIRONMENTS (1 atm)

Exposure Time	Equivalent $\Delta T$ at 2073 K in Kelvins			
	Hydrogen	Helium	Nitrogen	Argon
h				
1	+ 3	+ 5	+ 4	+ 9
50	+ 4	+ 6	+ 6	+ 9

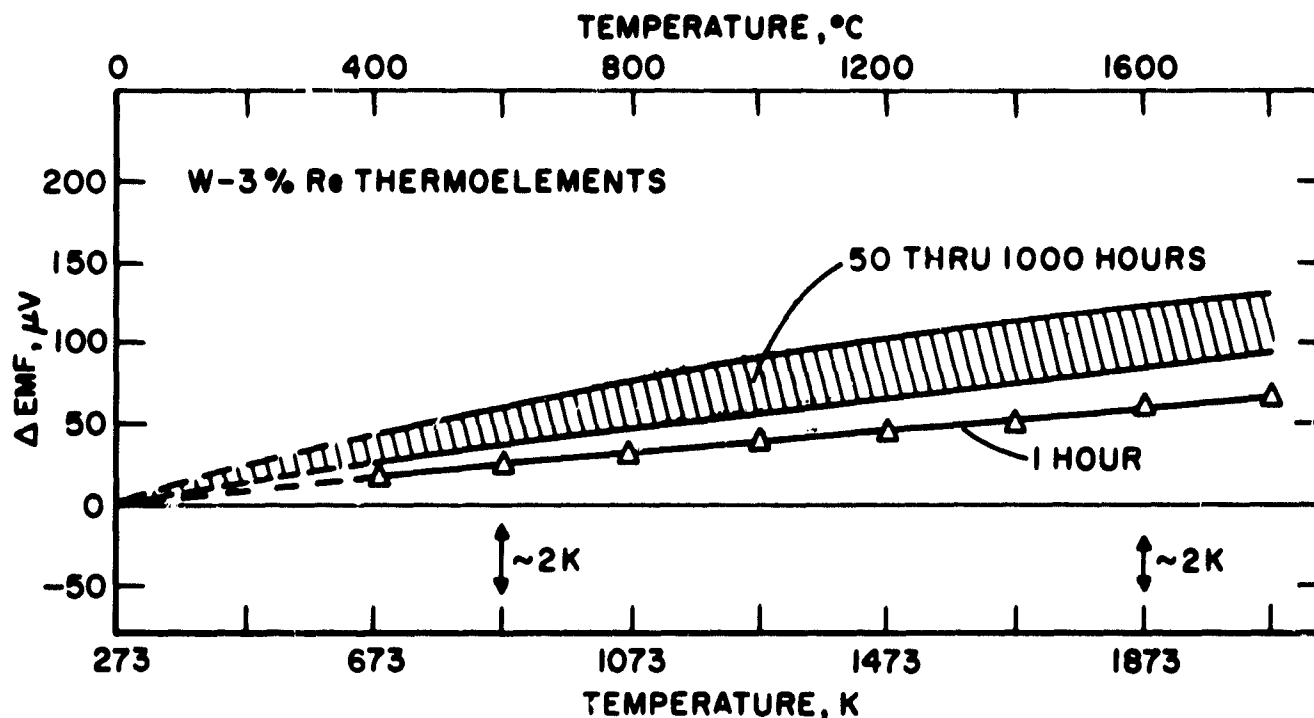


Figure 3. Change in the emf-temperature relationship of W-3% Re thermoelements from one lot after thermal exposure at 2400 K in nitrogen for 1, 50, 100, 150, 250, 500, 750 and 1000 hours. With the exception of the 1 hour data, all of the data fell within the cross-hatched area, with no significant trend with increasing exposure time.

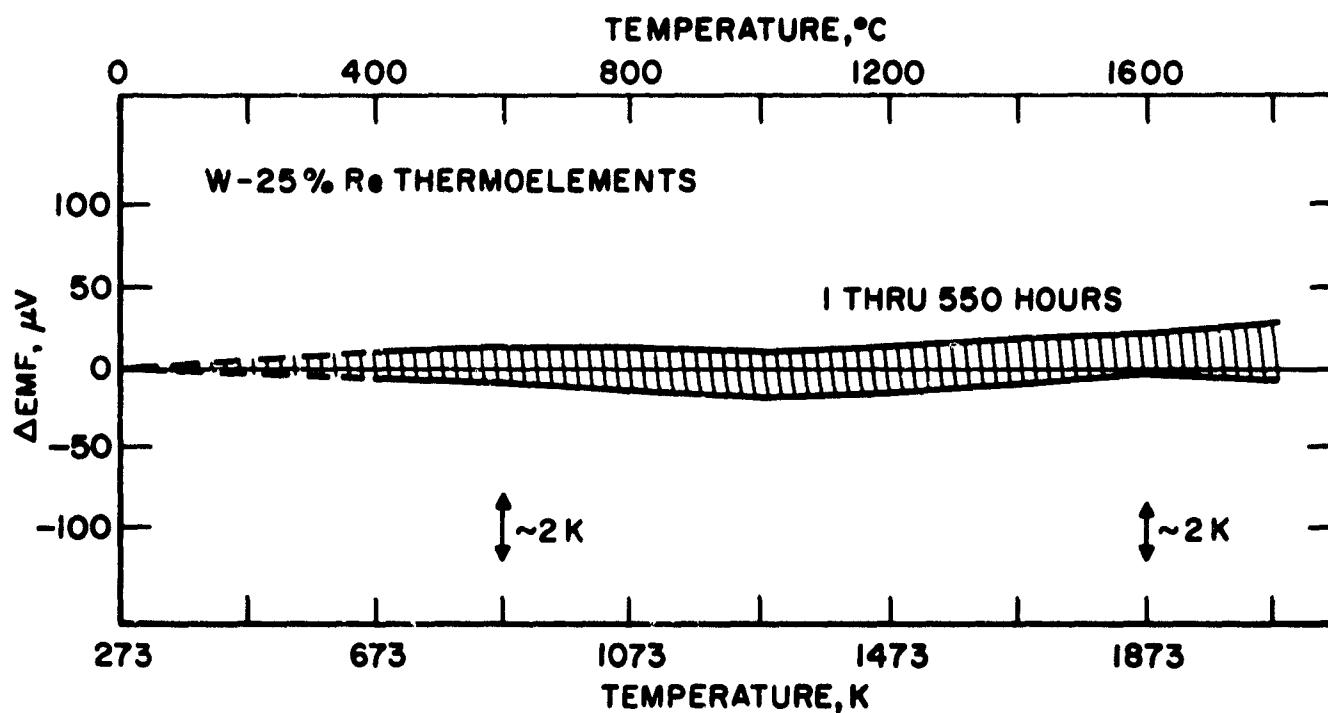


Figure 4. Change in the emf-temperature relationship of W-25% Re thermoelements from one lot after thermal exposure at 2400 K in nitrogen for 1, 50, 100, 150, 250, 500 and 550 hours. All of the data fell within the cross-hatched area, with no significant trend with increasing exposure time.

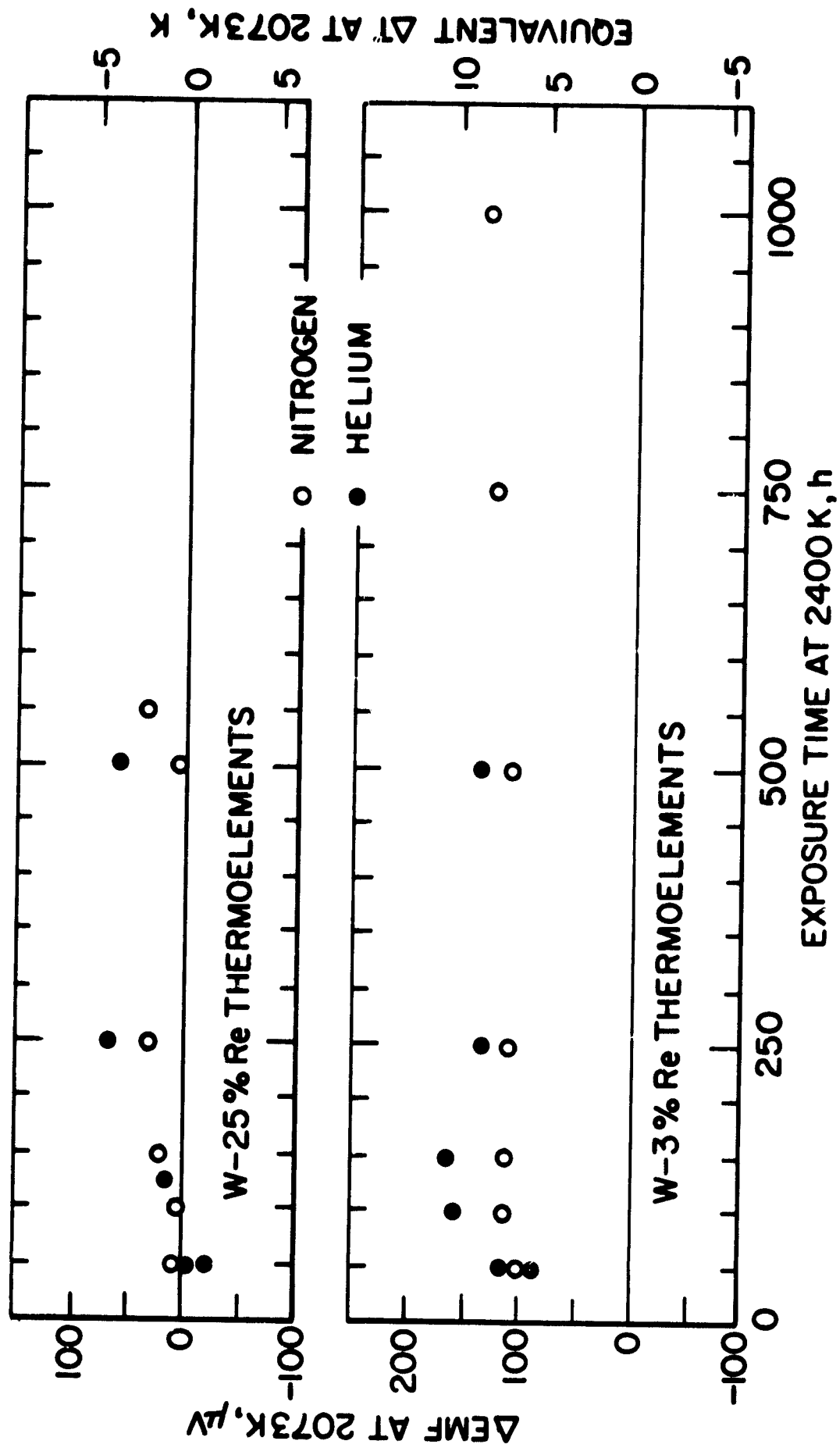


Figure 5. Change in the thermal emf at 2073 K of W-3% Re and W-25% Re thermoelements from one lot as a function of the exposure time at 2400 K in nitrogen or helium.

Aging studies ("shift"). An initial shift in the emf-temperature relationship with high temperature exposure of the thermoelements has been observed in these studies for several different lots of wire. It was desirable, therefore, to determine the time-temperature parameters required to essentially remove the initial shift, and hence age the thermoelements. For this study, thermoelements were exposed to temperatures ranging from 1200 to 3000 K and for time periods ranging from 2 minutes to 50 hours. The tests were performed in argon and in hydrogen (1 atm) with W-3% Re and W-25% Re thermoelements from the special lots of wire which had not received the usual heat treatment normally given by thermocouple suppliers (see section on MATERIALS TESTED).

In Fig. 6, the changes in the emf at 2073 K of the W-3% Re thermoelements (relative to an "as received" thermoelement from the same lot) after aging in argon and hydrogen for 1 hour are plotted as a function of the aging temperature. Above about 2200 K the change in the thermal emf is essentially independent of the aging temperature for a 1 hour exposure period. Further, the change in thermal emf of thermoelements aged in hydrogen is somewhat less than that of thermoelements aged in argon (about 100  $\mu$ V or 10% of the change in argon). The time dependency of the change in thermal emf of the W-3% Re thermoelements is shown in Fig. 7 for aging in argon at temperatures of 1400, 2000, 2200 and 2400 K. About 90% of the change in emf occurs after exposure for 2 minutes at 2400 K, or for 1 hour at 2000 K. At 1400 K, a gradual and continual change in thermal emf occurs, and extrapolation of the curve indicates that aging for about 1000 hours at this temperature would be required to complete 90% of the change (shift) in thermal emf. The time dependency of the change in thermal emf for aging in hydrogen exhibits similar behavior, and is shown in Fig. 8. If we define a time  $\tau$  as the time in minutes required at a given temperature T (in kelvins) to complete 90% of the shift in a given environment, then for times greater than 2 minutes and temperatures above 2000 K,  $\tau$  for the W-3% Re thermoelements from this particular lot is approximated by

$$\begin{aligned}\tau &= (6.97 \times 10^{-34}) (3500 - T)^{11} \text{ minutes} && (\text{Argon}), \\ \tau &= (1.35 \times 10^{-59}) (3500 - T)^{19} \text{ minutes} && (\text{Hydrogen}).\end{aligned}$$

The changes in emf at 2073 K of the W-25% Re thermoelements after aging in argon and hydrogen for 1 hour are plotted as a function of the aging temperature in Fig. 9. In contrast to the W-3% Re thermoelement, a relatively small shift (about -160  $\mu$ V at 2073 K) occurs with aging for 1 hour at temperatures above 1900 K. No significant difference in the thermoelectric characteristics of the W-25% Re thermoelements with aging in the different environments was found. The time dependency of the change in thermal emf of the W-25% Re thermoelements for aging temperatures of 2000 K and 2400 K is shown in Fig. 10. A few minutes at 2400 K in either argon or hydrogen is sufficient to virtually eliminate the initial shift in thermal emf. The shift observed for this lot of wire is opposite in direction to that observed for most of the lots of commercial W-25% Re thermocouple quality wire (see also ref. 1). These lots (a total of seven have been tested) have typically exhibited a small positive shift of less than 150  $\mu$ V at 2073 K after being aged at 2400 K in argon.

Remarks concerning aging. The special lots of W-3% Re and W-25% Re wires obtained from the wire manufacturers, when aged and formed into a thermocouple, exhibited an emf-temperature relationship that complied with the calibration table (refs. 7 and 8) of the commercial thermocouple wire suppliers to within the equivalent of  $\pm 1\%$  of the temperature. Since the thermoelements used in the aging study did not receive the usual annealing by the thermocouple supplier, the shifts observed are larger than one would expect to observe in commercial thermocouple quality wire. Undoubtedly, the large shift in the W-3% Re wire is primarily the result of removing the stresses that were introduced during the manufacturing processes. In the case of the W-25% Re wire, we suspect that the heat treatment it received after drawing (see section on MATERIALS TESTED) might have been sufficient to at least partially stress-relief the wire, and thus only a relatively small shift occurs.

If further aging to remove the residual shift in 0.25 mm diameter commercial W-3% Re and W-25% Re thermocouple wires (obtained from thermocouple suppliers) is desired, the time-temperature parameters presented here will probably be more than sufficient in most instances. For a particular lot of wire, the time-temperature parameters for thermal aging are expected to be dependent upon its previous thermal and metallurgical history. The amounts and nature of the chemical impurities present in the wires must also be considered. The small differences in the shift that were observed for the W-3% Re thermoelement after exposure in different environments indicates that some various small chemical changes in

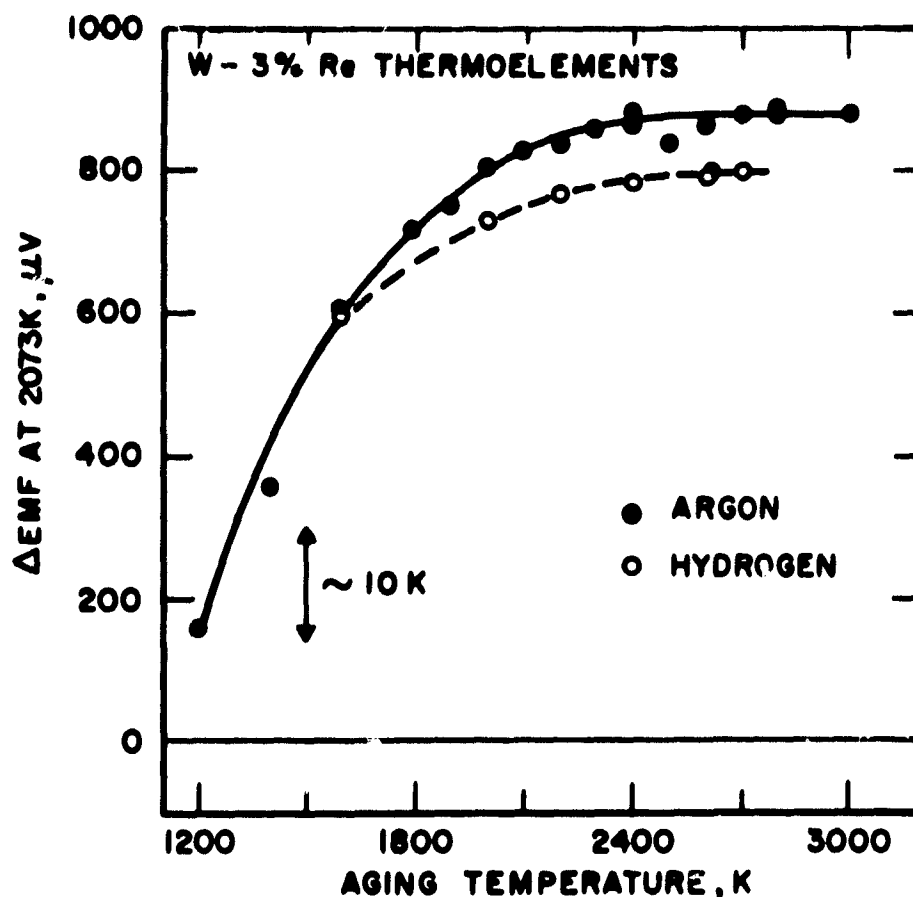


Figure 6. Change in the thermal emf at 2073 K of W-3% Re thermoelements from one lot as a function of the aging temperature in argon or hydrogen. The aging time was 1 hour for each thermoelement at the indicated temperature.

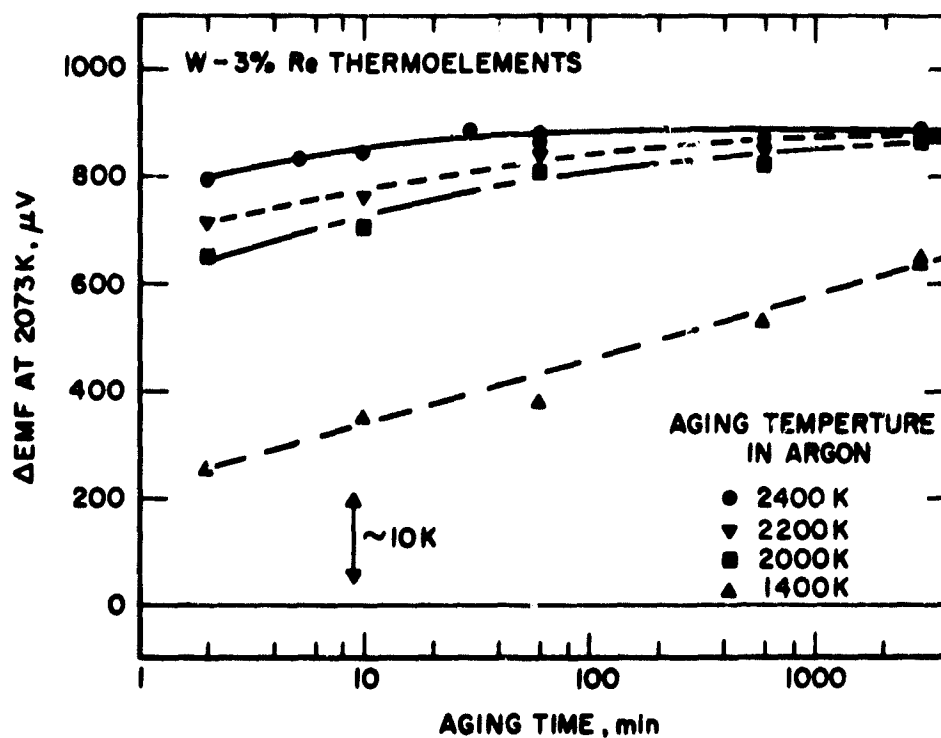


Figure 7. Change in the thermal emf at 2073 K of W-3% Re thermoelements from one lot as a function of the aging time in argon at the indicated temperature.

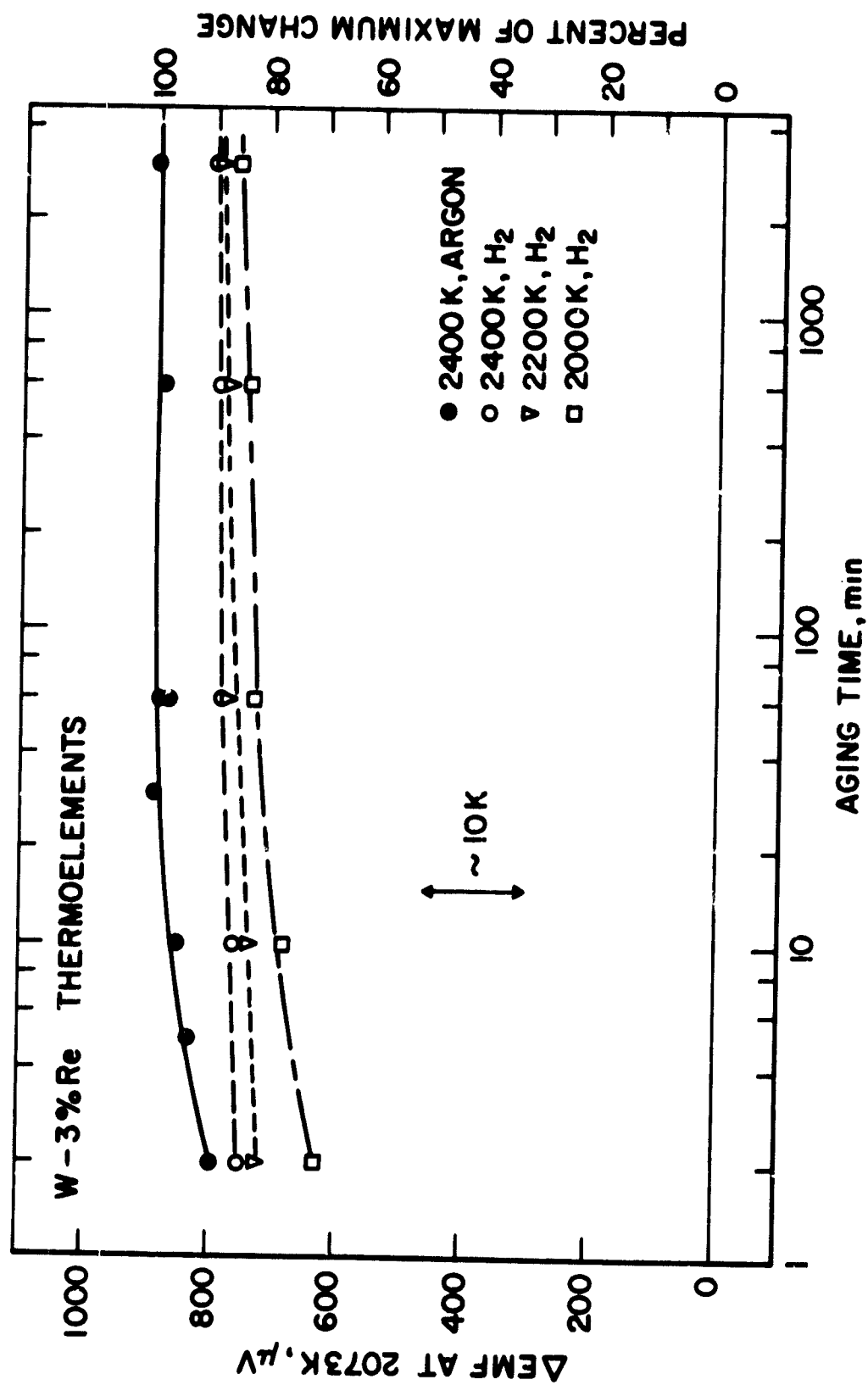


Figure 8. Change in the thermal emf at 2073 K of W-3% Re thermoelements from one lot as a function of the aging time in hydrogen or argon at the indicated temperature.

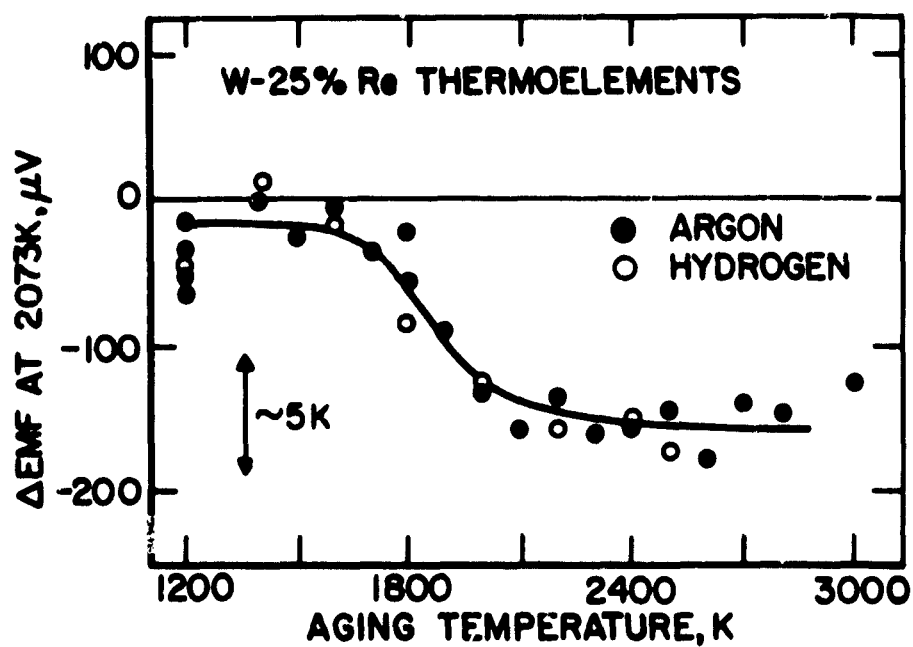


Figure 9. Change in the thermal emf at 2073 K of W-25% Re thermoelements from one lot as a function of the aging temperature in argon or hydrogen. The aging time was 1 hour for each thermoelement at the indicated temperature.

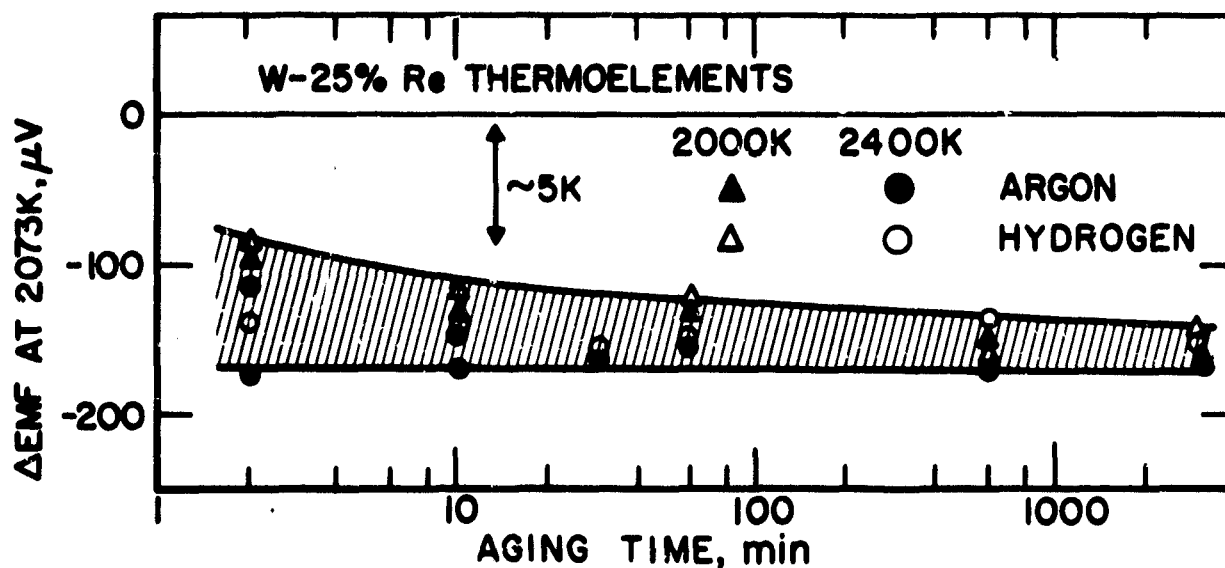


Figure 10. Change in the thermal emf at 2073 K of W-25% Re thermoelements from one lot as a function of the aging time in hydrogen or argon at the indicated temperature.

the wire most likely occur during the aging process. However, the routine chemical analyses that have been performed thus far have not been sufficient to substantiate this.

It is evident from these studies that unaged thermoelements subjected to temperatures in the range 1200 to 2000 K age at a rather slow rate. Thermocouples comprised of unaged thermoelements would be unstable during use in this temperature range. When used at higher temperatures they would also experience a continual gradual change in their emf-temperature relationship due to aging of portions of the thermoelements in the temperature gradient zone. Although the effect may be quite small after the first few hours of use, the emf-temperature relationship of the thermocouple becomes dependent upon the temperature distribution along the thermoelements, since inhomogeneities are introduced by the different aging conditions that exist along the thermoelements. Significant errors can then arise if the temperature distribution along the thermoelement changes during subsequent use. Properly aging the thermoelements before use would eliminate the possibility of errors introduced in this manner (although inhomogeneities may be introduced during use for other reasons).

Test with other W-Re alloy thermoelements. These tests were performed with the thermoelements of "doped" tungsten, "doped" W-5% Re and "undoped" W-5% Re, and with the W-25% Re thermoelement<sup>14</sup> that formed the "matching" negative thermoelement for these three thermoelements. The thermoelements were uniformly exposed in the test chamber at 2400 K for exposure periods up to 500 hours. All tests were performed in an argon environment. In Fig. 11, the change in the thermal emf at 2073 K for thermoelements from one lot of each type is plotted against exposure time at 2400 K. All the thermoelements experienced a positive initial shift in emf, which within experimental uncertainty is complete after 50 hours of exposure at 2400 K. After the initial shift, the thermoelements experienced no significant further change (drift) in thermal emf for exposure periods up to 500 hours.

For the positive thermoelements (W and W-5% Re), the initial shift in thermal emf at 2073 K is relatively large, ranging from about +400  $\mu$ V ( $\Delta T$  about +22 K) for the "doped" W thermoelement to about +500  $\mu$ V ( $\Delta T$  about +36 K) for the "doped" and "undoped" W-5% Re thermoelements. For the negative thermoelement (W-25% Re), the shift in thermal emf is small, averaging about +125  $\mu$ V ( $\Delta T$  about -8 K) at 2073 K. The thermoelements all exhibited a small positive change in thermal emf (equivalent to 5 to 10 K) between 1 and 50 hours of exposure at 2400 K. Thermoelements from a second lot from the same supplier were also tested in argon at 2400 K, and they also exhibited shifts of the same magnitude.

The emf-temperature relationship of thermocouples, formed from uniformly aged thermoelements, differs substantially from the emf-temperature relationship of thermocouples formed from the unexposed "as received" thermoelements. The differences (or shift) at 2073 K for the various thermocouple pairs are given in Table IV. By comparison, seven matched lots of W-3% Re and W-25% Re thermoelements (from two different suppliers) have been examined in these studies thus far, and the shifts (at 2073 K) for the thermocouple pair have ranged from +2 to +18 K after aging in argon. In a typical thermocouple application (such as heating in a calibration furnace), thermocouples formed with the unaged thermoelements would, in general, exhibit smaller short-term shifts than those reported here (for a given lot of wire). Nevertheless, significant changes can be observed in thermocouples comprised of unaged thermoelements after initial exposure to high temperature: Thermocouples, formed with the various thermoelements, were installed in the calibration furnace and exposed in argon for a short period (10 minutes) to only 2073 K; after the exposure, positive changes in thermal emf equivalent to as much as 5 K at 1273 K were observed.

TABLE IV. AVERAGE SHIFT IN THE EMF-TEMPERATURE RELATIONSHIP AT 2073 K FOR W-Re TYPE THERMOCOUPLES FROM TWO MATCHED LOTS AFTER EXPOSURE FOR 50 HOURS AT 2400 K IN ARGON (1 atm)

Thermocouple Type	Equivalent $\Delta T$ at 2073 K in Kelvins	
	Lot 1	Lot 2
"doped" W versus W-25% Re	+ 15	+ 23
"doped" W-5% Re versus W-25% Re	+ 26	+ 33
"undoped" W-5% Re versus W-25% Re	+ 27	+ 30

<sup>14</sup>The negative thermoelement is, for some thermocouple combinations, designated by the thermocouple supplier as W-26% Re (see section on MATERIALS TESTED).

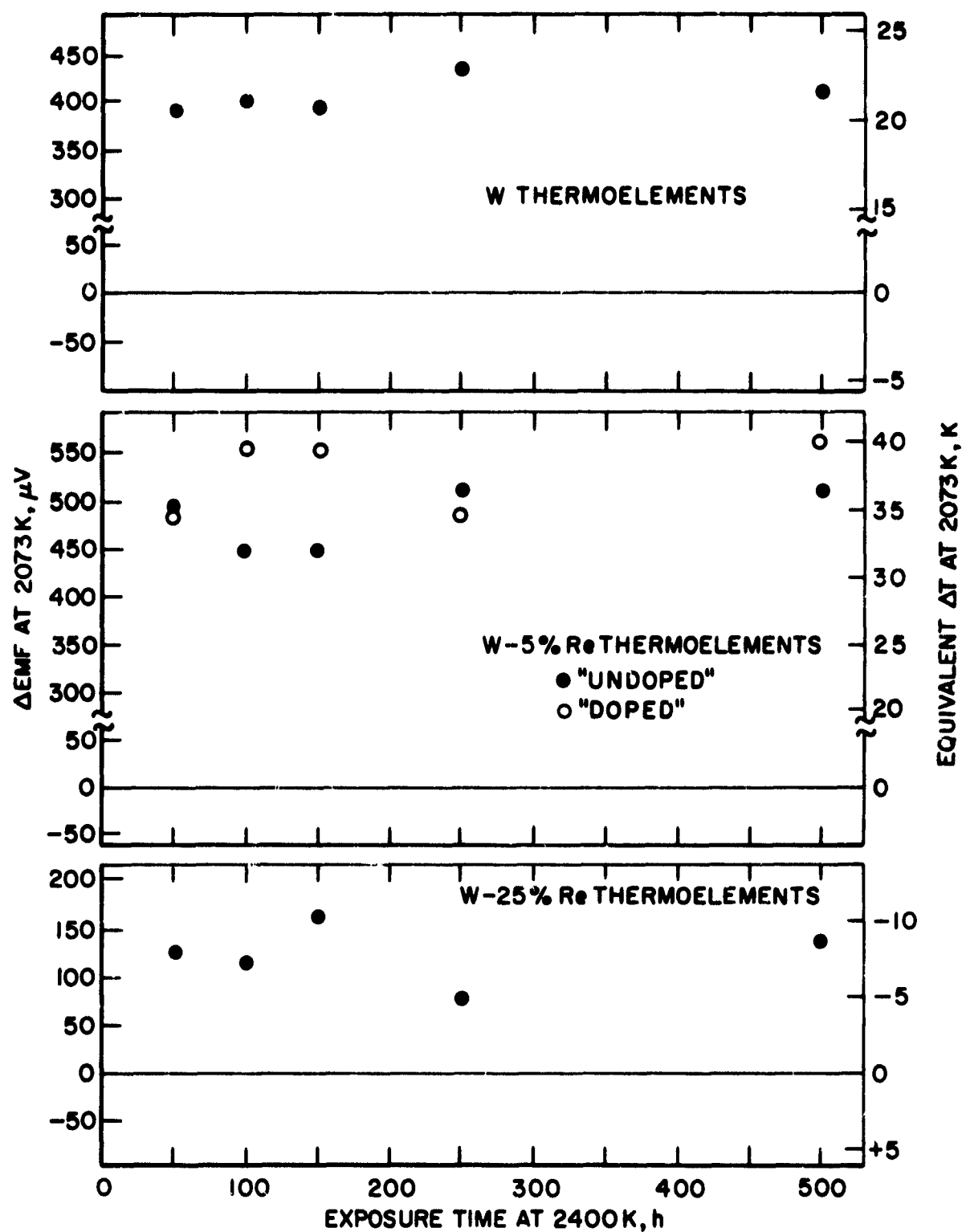


Figure 11. Change in the thermal emf at 2073 K of "doped" W, "doped" W-5% Re, "undoped" W-5% Re and W-25% Re thermoelements from one lot as a function of the exposure time at 2400 K in argon.

**Metallurgical observations.** An important consideration in the aging process is the change in the metallurgical structure of the alloys that occurs, since large decreases in the room temperature ductility can result. For typical applications, the thermoelements must be sufficiently ductile subsequent to the aging process to permit reliable thermocouple fabrication and installation. A simple test, consisting of attempting to coil the exposed thermoelements around a mandrel of known diameter, was performed on the aged thermoelements to give a semi-quantitative measure of their bend ductility at room temperature.

The W-3% Re thermoelement is a "doped" alloy. With exposure to high temperatures, the "dopants" modify the metallurgical structure as illustrated in Fig. 12. The results are for thermoelements taken from the same lot of wire<sup>15</sup> and then exposed in argon for a period of 1 hour. For temperatures up to 2600 K, grain growth is inhibited and only a slight modification in the fibrous grain structure occurs. The small-grained structure shown for the thermoelement exposed at 2400 K is similar to that reported previously (ref. 1) for W-3% Re thermoelements exposed for 50 hours or longer in argon at 2400 K. In that study, exposure for periods up to 1000 hours produced no further observable change in the grain structure. It therefore appears that the grain structure is stabilized after 1 hour exposure at 2400 K in argon. With exposure at 2700 K or above for 1 hour in argon, extremely large interlocking elongated grains develop rapidly as shown in Fig. 12. Typically the grains are one-half or a full wire diameter in width and many wire diameters long.

The W-3% Re thermoelements aged below 2600 K were quite ductile in that coiling of the thermoelements for many turns around a 1 mm diameter mandrel was usually possible. The thermoelements aged at 2700 K or above gave variable results in ductility, and in most cases it was not possible to coil the thermoelements one full turn around the 1 mm diameter mandrel. For aging of the W-3% Re thermoelement, it would therefore be desirable to retain the small-grained structure. Aging of the thermoelement for 1 hour in argon at 2400 K ensures this and is also sufficient to stabilize the wire thermoelectrically (essentially complete the initial shift in the emf-temperature relationship).

For the W-25% Re thermoelement, full recrystallization occurs with short exposure at temperatures of about 1800 K or above and equiaxed grains are formed. With continued high temperature exposure the equiaxed grains grow rather rapidly and, as the grain size increases, the thermoelement becomes less pliable at room temperature. At grain sizes larger than about 25  $\mu\text{m}$  the thermoelement becomes rather fragile and it is not well suited for thermocouple assembly. Fig. 13 illustrates the grain growth that occurs in the W-25% Re wire with exposure for one hour in argon at various temperatures. Examples of the grain growth that occurs with long-time exposure (up to 1000 hours) at 2400 K were reported previously (ref. 1). Aging of the W-25% Re thermoelement for 1 hour at 2000 K or a few minutes at 2400 K, which is sufficient to essentially eliminate the initial emf shift, leaves the thermoelement fully recrystallized but with only a moderate amount of grain growth (average grain size less than 20  $\mu\text{m}$ ). Aged in this manner, the thermoelement is pliable enough at room temperature to be repeatedly coiled around a 20 mm diameter mandrel. When extreme pliability is required<sup>16</sup>, the average grain size should be kept to less than 5  $\mu\text{m}$  and aging for only a few minutes in the 1900 to 2000 K range is recommended. This procedure may leave the thermoelement with a small residual emf shift ( $< 100 \mu\text{V}$  or the equivalent of 6 K at 2073 K).

For the W-3% Re and W-25% Re thermoelements exposed at 2400 K in nitrogen and helium environments, the change in the microstructure was very similar to that described previously for exposure in argon at 2400 K (ref. 1). The "doped" W and "doped" W-5% Re thermoelements (exposed at 2400 K in argon) exhibited somewhat different behavior from the W-3% Re thermoelement. After 1 hour of exposure at 2400 K the grain structure was about the same as that exhibited by the W-3% Re thermoelement (see Fig. 12; 2400 K sample).

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<sup>15</sup>This lot of wire had not been given a prior stress-relief anneal (see section on MATERIALS TESTED).

<sup>16</sup>Excessive bending or other mechanical deformation of the thermoelements should be avoided whenever possible, since appreciable changes in their thermoelectric properties may occur.

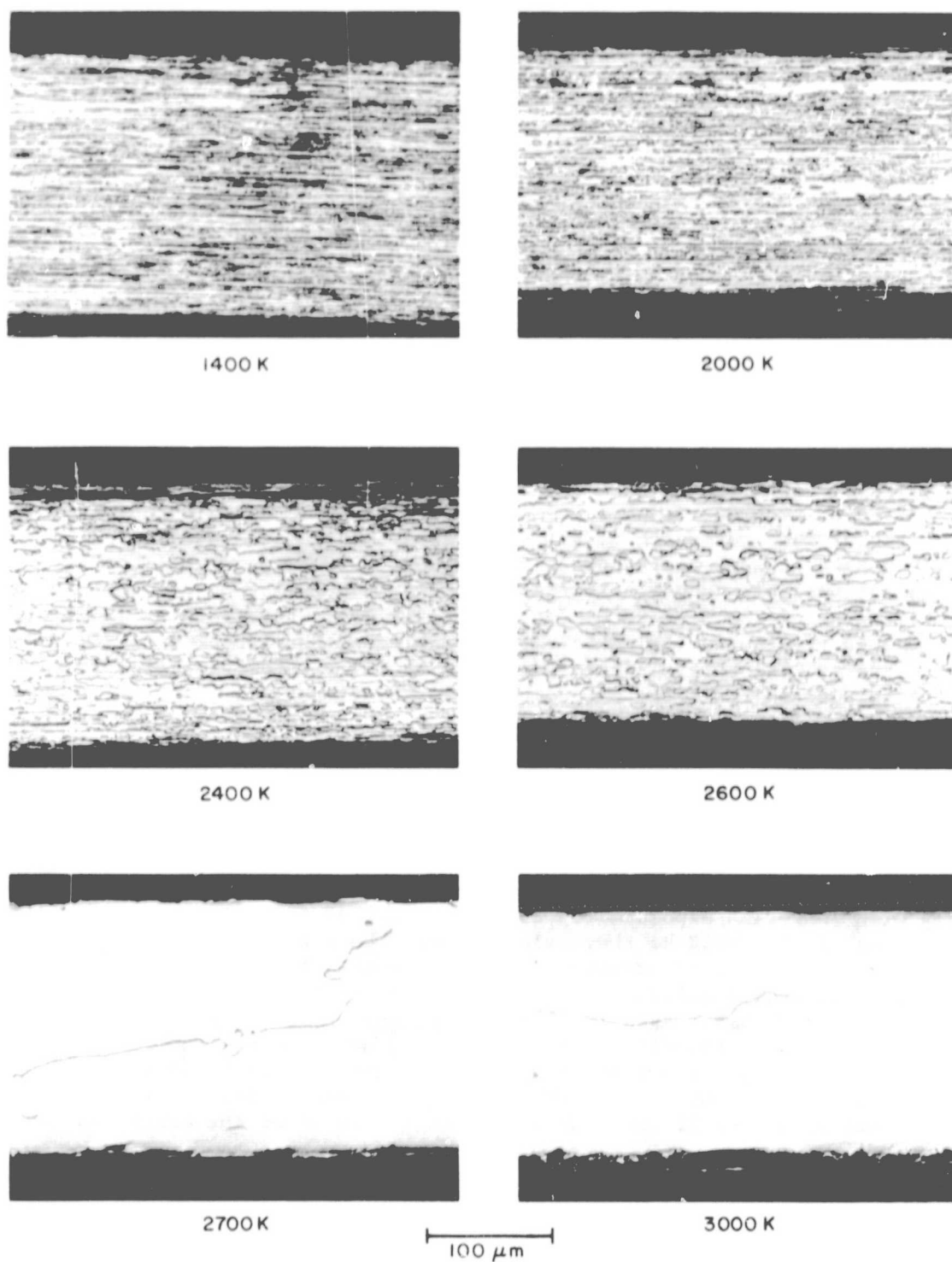


Figure 12. Typical microstructure of W-3% Re thermoelements from one lot after 1 hour of exposure in argon at the indicated temperature, as exhibited in a longitudinal cross-section. The thermoelement exposed at 1400 K exhibits little change in microstructure from the unheated "as received" condition.

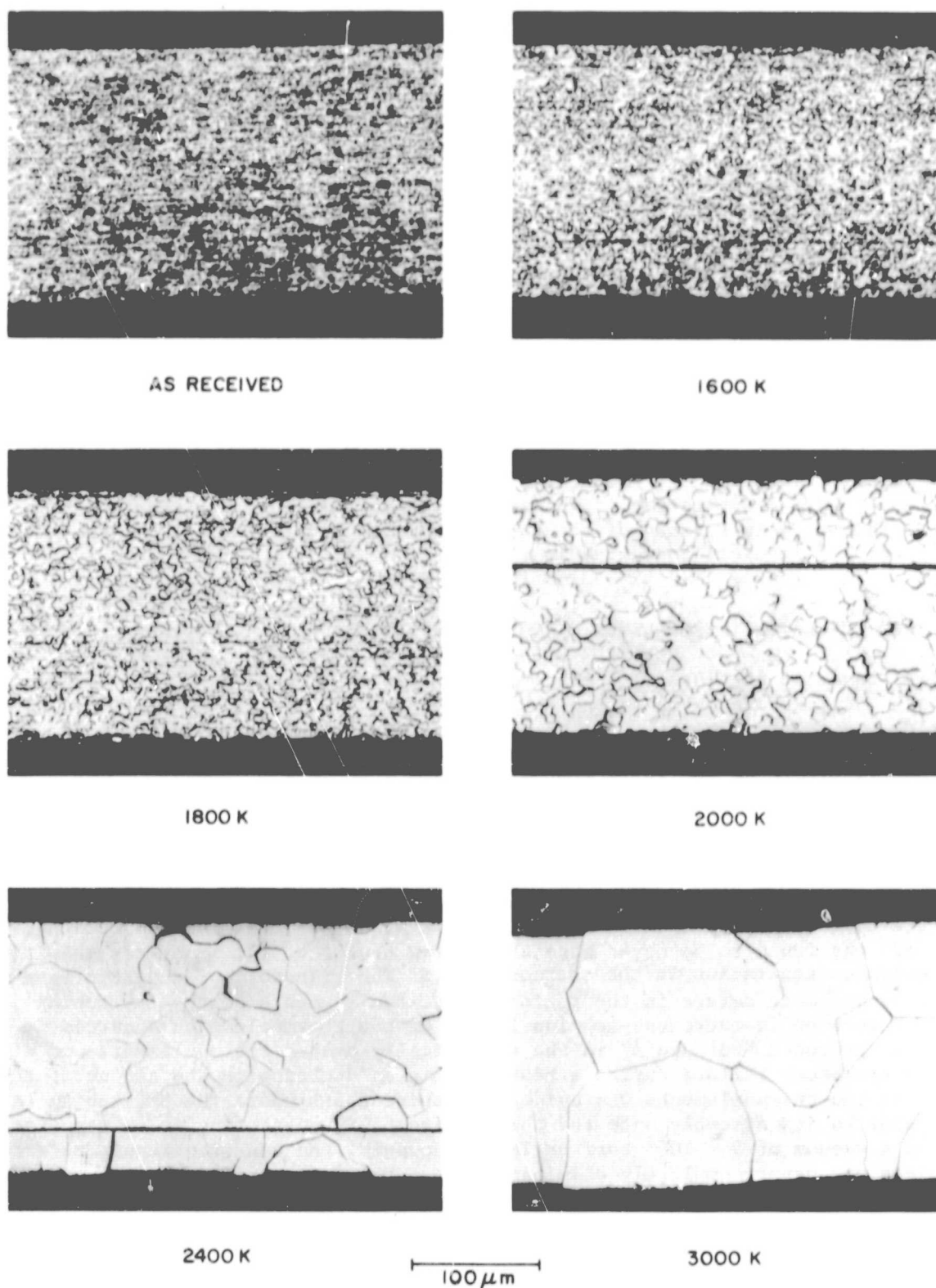


Figure 13. Typical microstructure of W-25% Re thermoelements from one lot after 1 hour of exposure in argon at the indicated temperature, as exhibited in a longitudinal cross-section. The dark line running longitudinally in some samples is a crack; detection depends upon orientation of sample.

However, the "doped" W and "doped" W-5% Re thermoelements exposed for periods in excess of 50 hours at 2400 K exhibited secondary recrystallization. Both of these thermoelements then exhibited a large interlocking elongated grain structure, similar to the structure shown in Fig. 12 for the W-3% Re thermoelements that were aged above 2600 K. In the "doped" W thermoelements, the formation of the larger grain structure resulted in a thermoelement that was brittle at room temperature; the "doped" W-5% Re thermoelement remained ductile in that it could be coiled around a 1 mm diameter mandrel.

In the case of the "undoped" W-5% Re thermoelement, small equiaxed grains, typically 10  $\mu\text{m}$  in diameter, were formed after one hour of exposure at 2400 K and the thermoelement was then brittle at room temperature. For exposure periods in excess of one hour, the subsequent grain growth was small, and after 500 hours the grain size was typically 30  $\mu\text{m}$ . In comparison, considerably larger grain growth occurred in the W-25% Re thermoelement, which exhibited grain sizes of the order of 100  $\mu\text{m}$  after exposure for 500 hours at 2400 K.

A number of the "as received" lots of wire exhibited cracks, which in some instances were one wire radius in depth. These cracks were not localized, but ran for long lengths along the wire (see Fig. 13). While they were more predominant in the W-25% Re thermoelement, where about one-half of the "as received" wire lots exhibited cracks, similar cracks were observed in a few lots of W-3% Re and W-5% Re thermoelements as well. While such cracks probably have no significant effect on the thermoelectric properties, they could conceivably lead to some structural problems. For example, forming reliable hermetic seals with such thermoelements can prove difficult. In addition, the cracks increase the effective surface to volume ratio of the thermoelement, which could make it more susceptible to effects of chemical contamination.

#### TESTS WITH BeO-INSULATED THERMOELEMENTS AND THERMOCOUPLES.

Material behavior in tests with electrically heated thermoelements. A series of tests were run with BeO-insulated W-3% Re and W-25% Re thermoelements by the method of electrically heating the thermoelements. All of the tests were run in argon (1 atm) at nominally 2000 K for 50 hours and the time-temperature parameters for degassing the BeO insulating tubing were varied between the tests (see section on EXPERIMENTAL APPARATUS AND PROCEDURES). The tests resulted in the following general characteristics. First, a gradual change in the resistance of the W-3% Re and W-25% Re thermoelements occurred during the exposure, making temperature control during the tests difficult. After the tests, it was found that tungsten and a small quantity of rhenium had been deposited for the most part as a coating upon the bore of the BeO tubing. The coating was present in the bore along the entire length of the tubing. Predominantly tungsten was transported; the rhenium concentration in the deposit was found to be never more than a few tenths of 1%; much less than the nominal rhenium concentration in the thermoelements. The transport of tungsten from the thermoelements was more severe in the regions where two segments of the BeO tubing joined; a localized reduction in the cross-sectional area of the thermoelements occurred in these regions. This produced "hot spots" in the electrically heated thermoelements and often led to their premature failure during a test. A marked decrease in the amount of tungsten transport from the thermoelements was evident in those tests where the BeO tubing was degassed, prior to its assembly onto the thermoelement, by subjecting it to temperatures up to 1800 K in a vacuum of  $5 \times 10^{-7}$  torr or less. However, the tungsten transport from the thermoelements was never completely eliminated.

When little or no high temperature degassing of the BeO tubing was performed, gross erosion of the W-Re thermoelements occurred. A typical example of the microstructure of two thermoelements which experienced gross erosion and yet remained intact for the 50 hours of exposure is shown in Fig. 14. The W-3% Re thermoelement had the fine-grained structure throughout, as was typical for thermoelements exposed bare in argon. However, this sample experienced up to a 10% reduction in diameter, and the surface had a roughened appearance, with the grain structure not clearly defined.

The W-25% Re thermoelement exhibited a porous surface layer, but unlike the W-3% Re thermoelement, no reduction in the diameter was detected. For the W-25% Re sample shown in Fig. 14, the surface layer is about 35  $\mu\text{m}$  deep. In the most successful tests, where

high temperature degassing of the BeO tubing was performed prior to testing, no surface layer was apparent, but there was still some transport of tungsten to the BeO tubing and the grains at the surface of the thermoelement showed a very definite rounding at their boundaries. From other metallographic observations on W-25% Re samples exhibiting only small surface layers, it was apparent that the pores enlarge along the grain boundaries. Since W is primarily being lost, the grains in the surface layer become Re enriched, and in some samples a second phase could be observed, most probably the W-Re sigma phase. In the center portion of the thermoelement, the usual large equiaxed grain structure was apparent in all cases.

For the two thermoelements whose microstructures are illustrated in Fig. 14, the rhenium concentration was determined across the transverse cross-section using electron probe microanalysis. For the W-3% Re thermoelement, the mean rhenium concentration was the same as for an unheated sample from the same lot, within the limits of detection. No significant increase in the Re concentration was detected near the edges<sup>17</sup> of the sample. The results for the W-25% Re thermoelement are presented in Fig. 15. In the center portion of the thermoelement, the mean rhenium concentration was again the same as for an unheated sample from the same lot, within the limits of detection. However, the rhenium concentration in the surface layer increases considerably, with rhenium concentrations as large as 45% being detected.

While no changes in rhenium concentration in the exposed W-3% Re thermoelement were detected by electron probe microanalysis, other evidence indicates that some tungsten is preferentially lost from the alloy. Qualitative spectrochemical analysis indicates that the coating in the bore of the BeO tubing is primarily tungsten, with much less than 3% of the coating as rhenium. Thermoelectric changes, to be discussed later, are in the expected direction for a slight rhenium enrichment of the alloy.

Spectrochemical analyses of representative specimens that were taken from the exposed thermoelements revealed no significant increase in the concentration of the metallic impurities. Consequently, chemical contamination of the thermoelements by metallic impurities transferred from the BeO tubing was not considered to be a serious problem in these tests.

In all of the BeO-insulated thermoelement tests that have been described in this section, degassing of the BeO tubing was performed in the test chambers, using the helical W-3% Re wire heater. Degassing in this manner was questionable, in that considerable doubt existed about the actual temperature attained by the BeO tubing as well as the temperature uniformity of the heat zone. This arrangement was used only for initial studies before the ultra-high-vacuum, high temperature furnace became available. Because many of the results described in this section later appeared to be unique to the method of high temperature exposure, it became important to conduct some additional tests using BeO tubing degassed under more favorable conditions.

Therefore, a test was performed where the BeO tubing was first degassed in the high temperature furnace, and a BeO-insulated W-25% Re thermoelement assembly was then exposed within the test chamber by the method of electrically heating the thermoelement. For the degas of the BeO tubing the furnace temperature was increased over a 5 hour period to about 1100 K, held at this temperature for about 20 hours, then increased during a 5 hour interval to about 1800 K where it was maintained for 4 hours. During most of the degas, the pressure in the furnace chamber was less than  $5 \times 10^{-8}$  torr (equivalent indicated nitrogen pressure), but occasionally it briefly increased to about  $5 \times 10^{-7}$  torr following an increase in the furnace temperature. The temperature was limited to 1800 K, since above this temperature serious warping of the BeO tubing was likely to occur. This degas schedule was consistent with those of the earlier tests which yielded the most successful results. After exposure of the BeO-insulated W-25% Re thermoelement assembly for 50 hours at 2000 K in argon, the thermoelement exhibited a surface layer of about 5  $\mu$ m, which was comparable to the more successful tests performed earlier. Again, the bore of the BeO tubing was tungsten coated.

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<sup>17</sup>Changes in the Re concentration within about 5  $\mu$ m of the edges (surface of thermoelement) are not readily detectable by the method of analysis used.

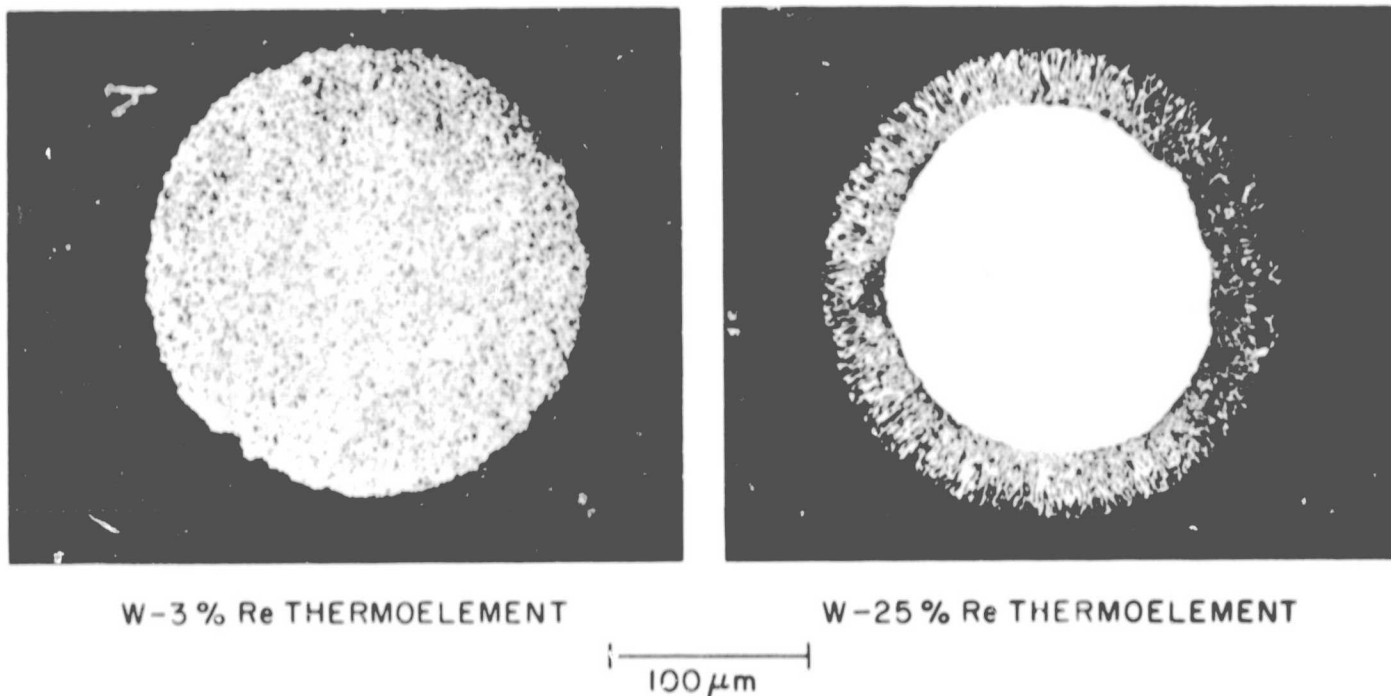


Figure 14. Examples of the microstructure of the thermoelements after exposure of the electrically heated BeO-insulated thermoelement assemblies at 2000 K in argon for 50 hours, as exhibited in a transverse cross-section.

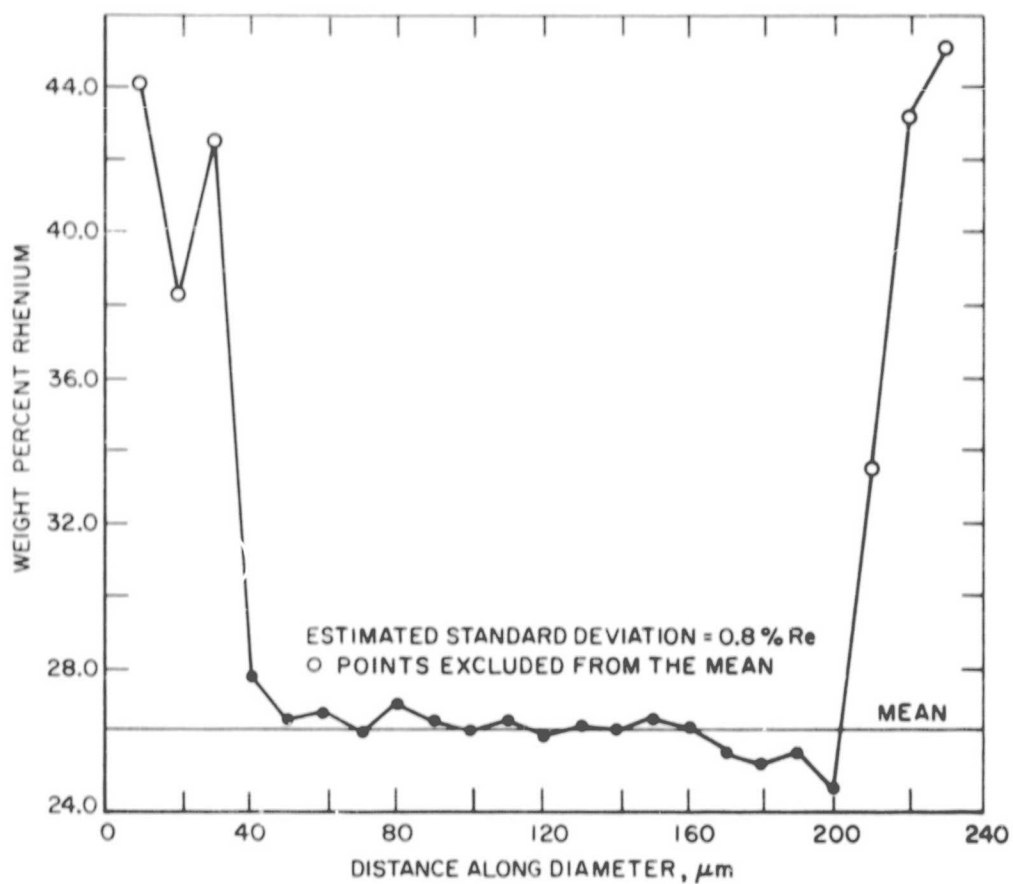


Figure 15. Re concentration across the transverse cross-section of the W-25% Re thermoelement, whose microstructure is given in Fig. 14. The Re concentration was determined by electron probe microanalysis.

Similar surface layers in the W-25% Re alloy have also been observed in carefully controlled tests by Wagner (ref. 9). Wagner exposed 1 mm diameter bare W-25% Re wires in oxygen atmospheres at pressures of  $10^{-5}$  to  $10^{-7}$  torr. After 700 hours in  $3 \times 10^{-5}$  torr  $O_2$ , he obtained a porous surface layer of about 80  $\mu$ m for wires exposed at 1920 K. Tungsten was preferentially lost as volatile oxides, and the W-Re sigma phase was found in the surface layer.

Material behavior for tests in the furnace. Tests were performed with BeO-insulated thermoelements using the high temperature furnace for both degassing of the BeO tubing and exposure of test samples. The time-temperature schedule for the degas of the BeO tubing in most of these tests was essentially the same as that described in the previous section. This schedule should not be construed as an optimum procedure. It was adhered to only because a comparison was desired with the results obtained for BeO-insulated thermoelements that were exposed by electrical heating of the thermoelements. Distinct differences in material behavior with the two methods of thermal exposure were found. For the BeO-insulated thermoelements exposed in the furnace for 50 hours at 2000 K in argon (1 atm), chemical attack of the thermoelements was negligibly small. In the case of the W-25% Re thermoelements, no porous surface layer occurred, and for most part the surfaces had essentially the same appearance as for a non-insulated thermoelement exposed in argon. A very slight amount of chemical attack on the surface was noted, however, at regions near the ends of BeO tubing segments. For the W-3% Re thermoelements, there was no visual evidence of any degradation. In addition, in all of these tests the bore of the BeO tubing remained free of any visible coating.

Two special tests were performed in the furnace with BeO-insulated W-25% Re thermoelements. For the first test, the BeO tubing was degassed in the test chamber with the helical wire heater employed in the early tests, and for the second test no high temperature degassing of the BeO tubing was performed. After both of these tests, the bore of the BeO tubing was again free of any visible coating, and most of surface of the thermoelements exposed within the BeO tubing was again similar in appearance to that of bare (non-insulated) thermoelements exposed in argon. However, at approximately 5 mm intervals, the thermoelement was fused to the inner bore of the BeO tubing. The fusion regions occurred alternately on opposite sides of the bore. While the thermoelement normally remains straight after a test, in these two tests its shape was distorted by the adhesion to the BeO. If such adhesion of the thermoelement to the BeO should occur in a sensor during use, it could conceivably lead to mechanical failure, particularly if frequent thermal cycles between widely differing temperatures should occur.

The results described in this section (i.e., the absence of a surface layer in the W-25% Re thermoelement, no reduction in diameter of the W-3% Re thermoelements, and the absence of a W coating in the bore of the BeO tubing) suggest that the difference in the material behavior from the results obtained in the previous section is due primarily to the different method of thermal exposure, and not due to the difference in the degassing technique of the BeO. It is apparent, however, from all of the tests performed that high temperature degassing of the BeO tubing enhances the BeO-thermoelement performance. Therefore some degassing of the BeO tubing is considered essential; especially in those cases where extended usage at elevated temperatures is sought. Dissolved, chemisorbed and occluded oxygen-containing gases (such as  $H_2O$ , CO, and  $CO_2$ ), formed during sintering of the BeO, can be released during subsequent use at elevated temperatures (ref. 10). In tests where the thermoelements were electrically heated, the tungsten (and some rhenium) is probably removed as a volatile oxide. Similarity of the porous surface layers with those obtained in the tests by Wagner (ref. 9) tend to confirm this. It may be that the chemical reaction and subsequent tungsten transport is hastened by the radial temperature gradient that exists at the BeO-thermoelement interface.

Long-term material compatibility. A thermocouple drift test, performed in the high temperature furnace for 1029 hours, exposed BeO-insulated W-3% Re versus W-25% Re thermocouples at 2073 K in argon while in the presence of Ta. Prior to the drift test, both the thermoelements and the BeO insulating tubing were given preparatory heat treatments. The thermoelement preparation consisted of a vacuum degas at 1570 K followed by aging in argon at 2400 K in order to essentially eliminate the initial shift in the thermal emf. The BeO tubing was degassed in the furnace with a degas schedule similar to that described previously (see page 27). After installation in the furnace, the BeO insulated thermocouples

were vacuum degassed in situ with 2 hour exposures at temperatures of 1000, 1100 and 1300 K. The furnace was then cooled and back-filled with argon for the drift test.

After exposure for 1029 hours at 2073 K in argon, no gross degradation of the thermoelements, BeO tubing, or tantalum was observed. However, the BeO tubing had adhered to the tantalum at a region (confined to an area < 1 mm in diameter) near the entrance to the tantalum blackbody enclosure. Most likely this was one of the few places of intimate contact between the tantalum and the BeO. As in the previous tests in the furnace, there was no evidence of any serious chemical incompatibility between the thermoelements and BeO tubing. Effects such as changes in the wire diameter, porous surface layers in the W-25% Re alloy, and W coating in the bore of the BeO tubing were not observed. In the W-25% Re thermoelements, a very slight amount of attack on the wire surfaces was apparent at regions where small gaps (< 1 mm) occurred between adjacent BeO insulating sections within furnace hot-zone region; the attack was confined to the uncovered portions of the thermoelements. No evidence of similar behavior in the W-3% Re thermoelements could be found. The changes in the microstructure of the exposed thermoelements were, in general, typical of that observed in bare-wire studies; the small-grained structure was retained in the W-3% Re thermoelements and some growth in the equiaxed grains occurred in the W-25% Re thermoelements.

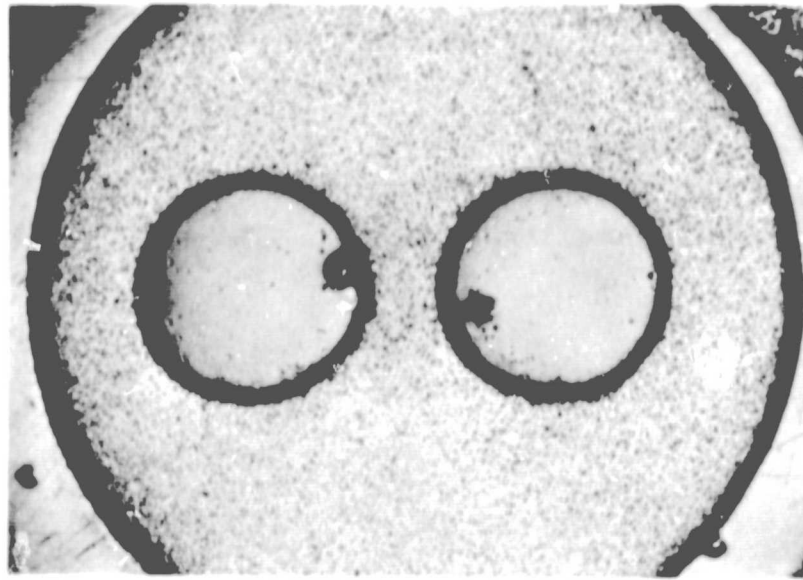
The portions of the BeO insulators that were in the hot-zone region of the furnace had attained a translucent appearance. Photomicrographs of BeO cross-sections revealed that the grain size of the translucent BeO tubing ranged from about 30 to 60  $\mu\text{m}$  (see Fig. 16). In contrast, the degassed BeO tubing did not show any change in grain size from the "as received" BeO tubing, where grain sizes were of the order of 1 to 5  $\mu\text{m}$ . (Growth of the BeO grains also occurred in a preliminary test that was performed, which exposed thermocouples at 2000 K for 214 hours in an environment of argon and tantalum). In samples of BeO tubing where grain growth was exhibited, it was noted that a 5 to 10% reduction in the diameter occurred. It is thought that this reduction is a result of densification. This would indicate that the density of the "as received" BeO was less than 95% of theoretical maximum density.

In the tests that exposed the BeO tubing to high temperatures with no tantalum present (50 hour tests in argon), no appreciable growth was apparent in the BeO grains and the BeO tubing remained opaque. To compare with these tests, a test was performed for 50 hours in the presence of tantalum (at 2073 K in argon). BeO tubing from this test had a similar appearance to the BeO tubing exposed in the presence of tantalum in the 214 hour and 1029 hour drift tests--the grain size ranged from about 10 to 25  $\mu\text{m}$  and the BeO was translucent. It therefore appears that the grain growth observed is influenced at least in part by the presence of tantalum. It may be that tantalum is acting as a getter, cleaning up much of the residual impurities in the BeO tubing. In refractory ceramics, grain growth may be either inhibited or promoted by the presence of small amounts of impurities (ref. 11). We suspect that the growth of the BeO grains is accelerated in this instance, due to a decrease in the impurity levels.

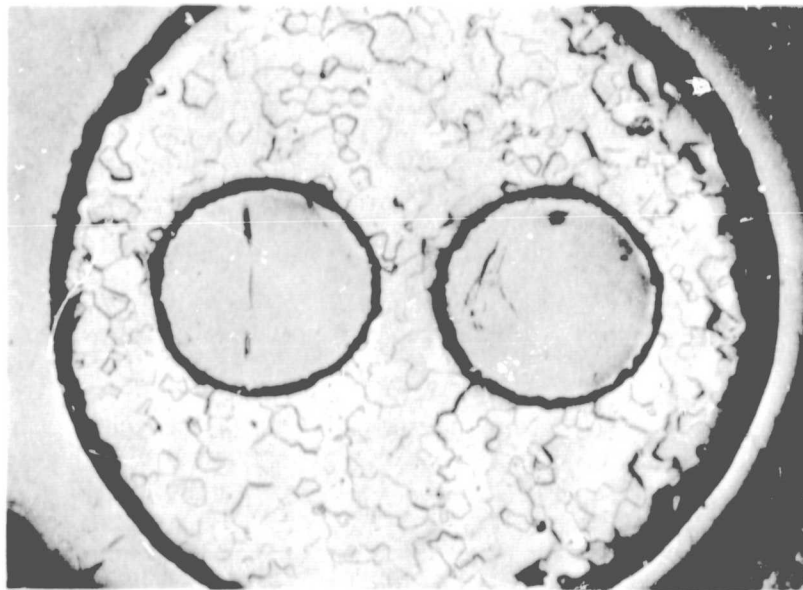
A spectrochemical analysis<sup>18</sup> of the BeO tubing was performed on the "as received" material, on degassed material, and on the materials exposed in argon in the presence of tantalum at 2000 K for 214 hours and at 2073 K for 1029 hours. Table V gives the principal impurities detected in these materials. In most cases there is a reduction in the impurity level as the material is degassed and then thermally exposed in argon in the presence of tantalum for extended intervals of time. The largest change that occurred with degassing was the removal of Si from 120 ppmw to below detection limits (about 2 ppmw). Ta and W were not detected in any of the samples, but are listed to emphasize the relatively high detection levels for these elements. The exposure of the BeO tubing in the 1029 hour test resulted in a reduction of the total detectable impurities by almost a factor of ten, to a total of 69 ppmw. Substantial changes in the impurity levels were detected for Al, Ca, and Mg; these elements had experienced little or no reduction in impurity levels after degassing. C and Na were also reduced by exposure in the presence of tantalum.

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<sup>18</sup>Carbon was determined by combustion-gas chromatography.



(a)



(b)

300  $\mu\text{m}$

Figure 16. Examples of the microstructure of sintered double-bore BeO insulating tubing (1.1 mm o.d., 0.3 mm bore) as exhibited in a transverse cross-section (a) after vacuum degassing at 1800 K, and (b) after exposure for 1029 hours at 2073 K in argon and in the presence of tantalum.

TABLE V. CHEMICAL ANALYSIS OF SINTERED, DOUBLE-BORE BeO INSULATING TUBING

(ppmw)

<u>Principal Impurities<sup>a</sup></u>	<u>"As received" material</u>	<u>Degassed material</u>	<u>Material exposed for 214 hours at 2000 K in argon in the presence of tantalum</u>	<u>Material exposed for 1029 hours at 2073 K in argon in the presence of tantalum</u>
Aluminum	200	300	90	15
Calcium	30	30	10	6
Carbon	230	115	42	42
Copper	ND (< 1) <sup>b</sup>	ND (< 1)	1	1
Iron	20	7	2	2
Magnesium	90	80	ND (< 1)	1
Nickel	2	ND (< 2)	ND (< 2)	ND (< 2)
Potassium	30	15	15	ND (< 2)
Silicon	120	ND (< 2)	ND (< 2)	2
Sodium	40	20	20	ND (< 2)
Strontium	ND (< 5)	10	ND (< 2)	ND (< 2)
Tantalum	ND (< 500)	ND (< 500)	ND (< 500)	ND (< 500)
Titanium	7	ND (< 5)	ND (< 5)	ND (< 5)
Tungsten	ND (< 500)	ND (< 500)	ND (< 500)	ND (< 500)
Total Detected Impurities	769	577	180	69

<sup>a</sup> Samples were analyzed for 42 metallic elements.<sup>b</sup> ND, not detected. The values in brackets are estimated detection limits.

Since the BeO tubing was of high purity, the degassing procedure used in the present work was designed primarily to remove sorbed gases and the procedure was limited to relatively moderate temperatures ( $< 1850$  K) to prevent gross physical changes in the tubing (such as warpage, grain growth and dimensional changes due to evaporation). Nevertheless, the above results demonstrate that the degassing was also effective in reducing some of the metallic impurity levels and it might be possible to derive a procedure which will further "purify" the BeO tubing as well. Droege, et. al. (ref. 12) reported achieving higher purity in sintered BeO insulating tubing after long term exposure in vacuum, and they report exposure of the tubing for 12 hours at about 2225 K to be effective in reducing the metallic impurities present.

Representative samples from the thermoelements that were exposed within the BeO tubing for 1029 hours at 2073 K were chemically analyzed by general mass spectrographic methods. The metallic impurities detected in the samples were at the same levels, within a factor of ten, as in the unexposed thermoelements from the same lots. Consequently, chemical contamination of the thermoelements by metallic impurities transferred from the BeO tubing or surroundings was not a serious problem.

Thermoelectric data for electrically-heated thermoelements. In the tests where the BeO-insulated thermoelements were exposed to high temperatures by electrically heating the thermoelements, it was sometimes possible to remove the thermoelement from the BeO tubing after the test. In these cases, the emf-temperature relationship of the exposed thermoelement versus an unheated "as received" thermoelement from the same lot (spool) was then determined in the calibration furnace. Typical results showing the change in the emf-temperature relationship of the W-3% Re thermoelements that were exposed for 50 hours (at nominally 2000 K in 1 atm of argon) are given in Fig. 17. Results for a thermoelement from the same lot that was exposed bare (without insulators) for 50 hours at 2000 K in argon is shown for comparison purposes. The curvature of the data for the BeO-insulated thermoelements is the reverse of that obtained in tests exposing bare-wire thermoelements in vacuum at 2400 K (ref. 1). The result is as expected, since for the BeO-insulated thermoelements W is lost preferentially, while for the thermoelements exposed bare in vacuum, Re is lost preferentially. It can be seen that the average difference in the emf-temperature relationship at 2073 K between the BeO-insulated W-3% Re thermoelements and the sample exposed without insulators is about  $-200$   $\mu$ V (equivalent  $\Delta T$  about  $-1.2$  K).

Similar results were obtained for the BeO-insulated W-25% Re thermoelements that were exposed by electrically heating the thermoelements, as illustrated in Fig. 18. The difference in the emf-temperature relationship from the bare-wire result was found to be proportional to the depth of the porous surface layer in the thermoelement. A transverse cross-section of the thermoelement that exhibited the largest change in its emf-temperature relationship (from the thermoelement exposed bare) is given in Fig. 14. For the thermoelement that showed the smallest change in its emf-temperature relationship, transverse cross-sections at three different points along the thermoelement showed no porous surface layer, although the grains at the surface of the thermoelement were clearly rounded at their boundaries, indicating some material loss had occurred. The thermoelements with intermediate changes in their emf-temperature relationship had surface layers up to  $10$   $\mu$ m in depth. Again, since W is preferentially lost from the thermoelements, the change in the emf-temperature relationship is in the opposite direction from that observed for W-25% Re thermoelements exposed bare in vacuum at 2400 K, where Re is lost preferentially. Neglecting the thermoelement with the largest change, the average difference in the emf-temperature relationship at 2073 K between the BeO-insulated W-25% Re thermoelements and the W-25% Re thermoelement exposed without insulators is about  $-240$   $\mu$ V (equivalent  $\Delta T$  of  $+15$  K).

If the average results for W-3% Re and W-25% Re thermoelements are combined, the emf at 2073 K of a thermocouple comprised from the thermoelements which were thermally exposed for 50 hours with BeO insulators minus the emf at 2073 K of a thermocouple comprised from thermoelements which were exposed bare (without insulators) would be equivalent to only about  $+3$  K. These results demonstrate that gross chemical and physical changes, when confined primarily to the surface of thermoelements, may have very little effect on their thermoelectric properties. Conversely, reasonable stability of the thermal emf of the thermocouple in use does not insure that gross chemical attack is not occurring.

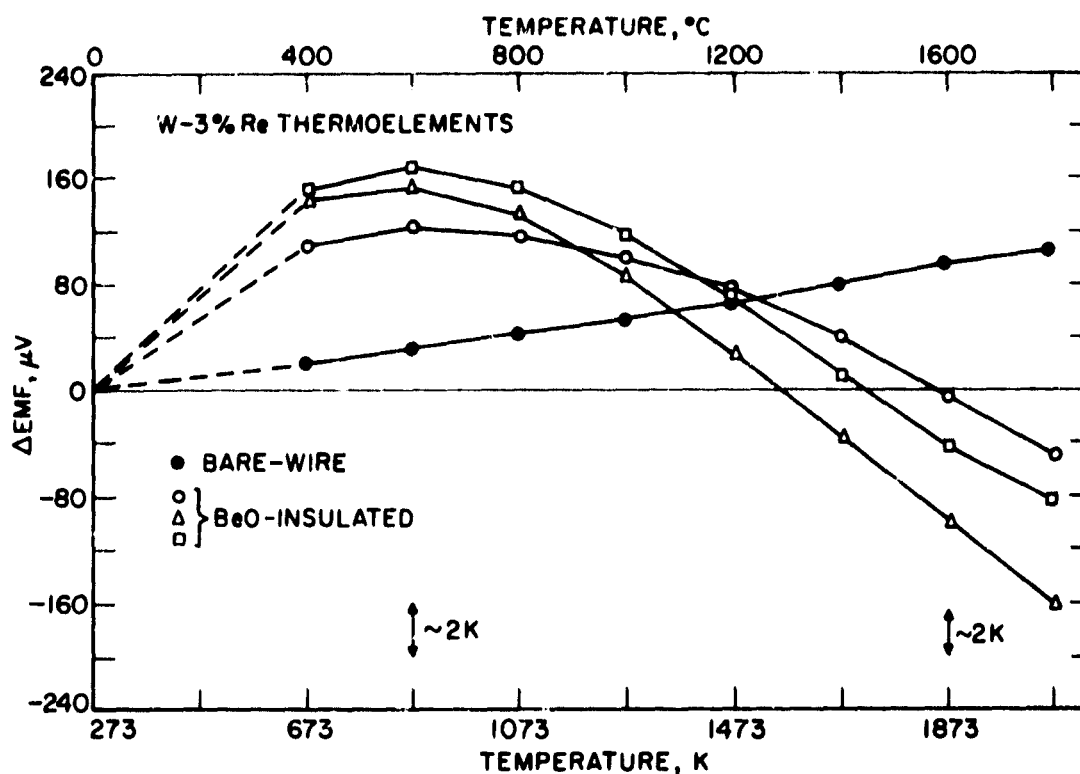


Figure 17. Change in the emf-temperature relationship of W-3% Re thermoelements exposed both with and without BeO insulators for 50 hours in argon at 2000 K. The thermoelements were all from the same lot and were exposed by the method of electrically heating the thermoelement.

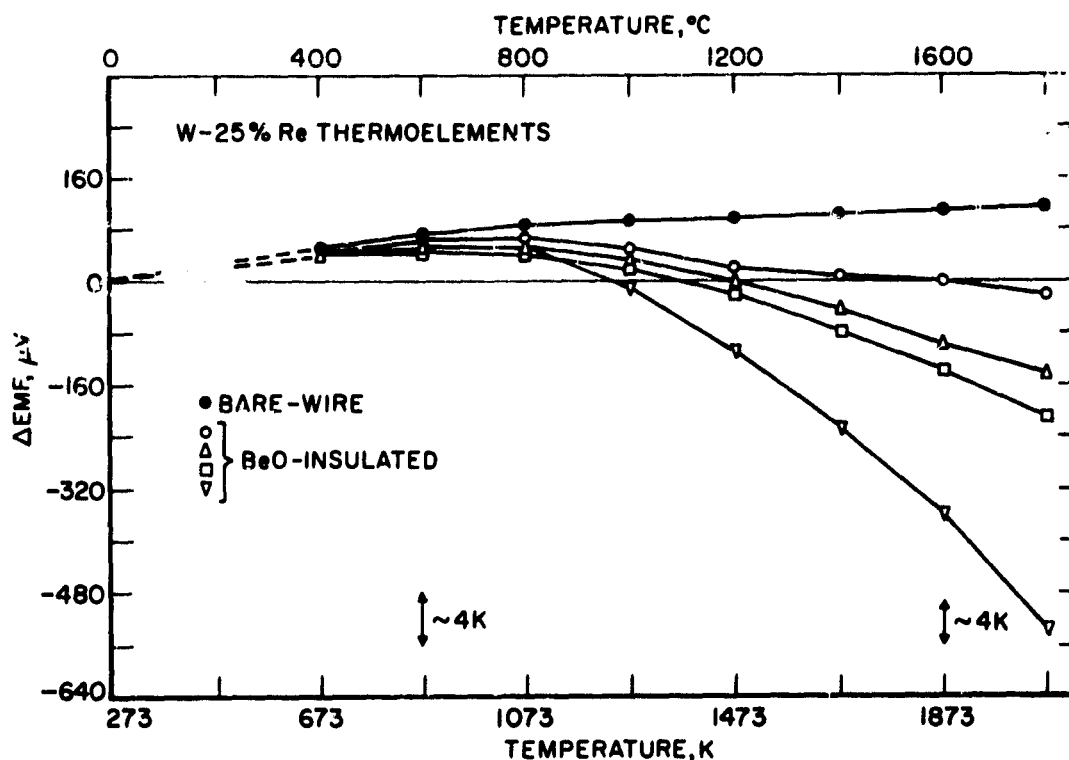


Figure 18. Change in the emf-temperature relationship of W-25% Re thermoelements exposed both with and without BeO insulators for 50 hours in argon at 2000 K. The thermoelements were all from the same lot and were exposed by the method of electrically heating the thermoelement.

Drift in thermal emf of BeO-insulated thermocouples. The thermal emf of three BeO-insulated W-3% Re versus W-25% Re thermocouples was measured about every 20 to 30 hours during the 1029 hours of exposure at 2073 K in argon (at 1 atm). The preliminary 214 hour test at 2000 K performed with four BeO-insulated W-3% Re versus W-25% Re thermocouples will not be discussed in detail, since comparable results were obtained. The tests were performed in the ultra-high-vacuum, high temperature furnace, with the thermocouples inserted into the tantalum blackbody enclosure previously described. The heat treatments of the materials prior to the test were discussed in the section on long-term material compatibility.

In order to analyze and present the data, the values of emf measured for each thermocouple during the course of the test were adjusted to correspond to 2073 K in accordance with the following:

$$\text{Thermocouple emf at 2073 K} = \text{Measured emf} - \Delta T \left[ \frac{dE}{dT} \right],$$

where  $\Delta T$  = (temperature determined with the optical pyrometer) - 2073 K, and  $\left[ \frac{dE}{dT} \right]$  = thermoelectric power of the thermocouple at 2073 K (about 15.8  $\mu\text{V/K}$ ).

The thermal emf of one thermocouple was monitored continuously throughout the test with a recorder, as a check on the temperature stability of the furnace. Both the thermocouple and the periodic measurements made with the optical pyrometers indicated that the temperature was stable within  $\pm 4$  K for the duration of test. Over a 24 hour period, the temperature stability was typically  $\pm 2$  K and for shorter periods (20 to 30 minutes),  $\pm 0.5$  K. The measurements made with the optical pyrometers indicated the average temperature was about 2070 K. Since the furnace temperature was closely controlled near 2073 K, the above adjustment of the measured emfs to the 2073 K equivalency could be made without introducing any appreciable uncertainty in the drift results by using an approximate value for the thermoelectric power of the thermocouples.

The thermal emf at 2073 K for one of the thermocouples is plotted against time of exposure at 2073 K in Fig. 19. The data presented are based upon the measurements made with the automatic photoelectric optical pyrometer. The curve through the data points is a straight line, which was fitted to the data by the method of least squares. All three bases of reference used in this test (two observers with the visual optical pyrometer and the automatic photoelectric optical pyrometer) indicated that the thermocouple experienced a small positive drift in its thermal emf at 2073 K equivalent to about 2.5 mK/h (or a 2.6 K total change in 1029 hours). The standard deviation of the residuals is equivalent to 0.4 K, and the standard deviation of the slope of the line is equivalent to 0.2 mK/h. The slope [2.5 mK/h], while small, is considered statistically significant, since it is more than three times the standard deviation of the slope. The behavior of the other two test thermocouples was almost identical, with each thermocouple exhibiting a small positive drift in its thermal emf at 2073 K equivalent to about 2.9 mK/h and 2.3 mK/h (or a 3 K and 2.4 K total change, respectively, in 1029 hours). The test results for all three thermocouples are summarized in Table VI.

The measuring junctions of the thermocouples were located at different levels (spaced about 2.5 cm apart) within the blackbody enclosure. However, the measured values of emf for the thermocouples agreed to within the equivalent of about 2 K throughout the entire test period. Consequently, it was concluded that the blackbody enclosure was reasonably uniform in temperature. The thermocouples used for the preliminary 214 hour test at 2000 K were installed in a similar manner, and similar temperature uniformity was indicated at 2000 K.

The ability to resolve a change in the calibration of a thermocouple at 2073 K by these methods over a period of 1029 hours depends primarily upon the stability and precision of the optical pyrometers and the constancy of the spectral transmittance of the furnace window. The calibrations of both the visual pyrometer and the photoelectric pyrometer employed in this test were checked at about 2060 K before, at the middle, and after the 1029 hour test by the Optical Radiation Section at NBS. Both pyrometers were intercompared with the NBS standard photoelectric pyrometer (ref. 13) using a vertical resistive-heated graphite blackbody as a transfer source. These checks indicated that no significant change occurred in the calibration of either instrument ( $\leq 0.5$  K for the photoelectric pyrometer and

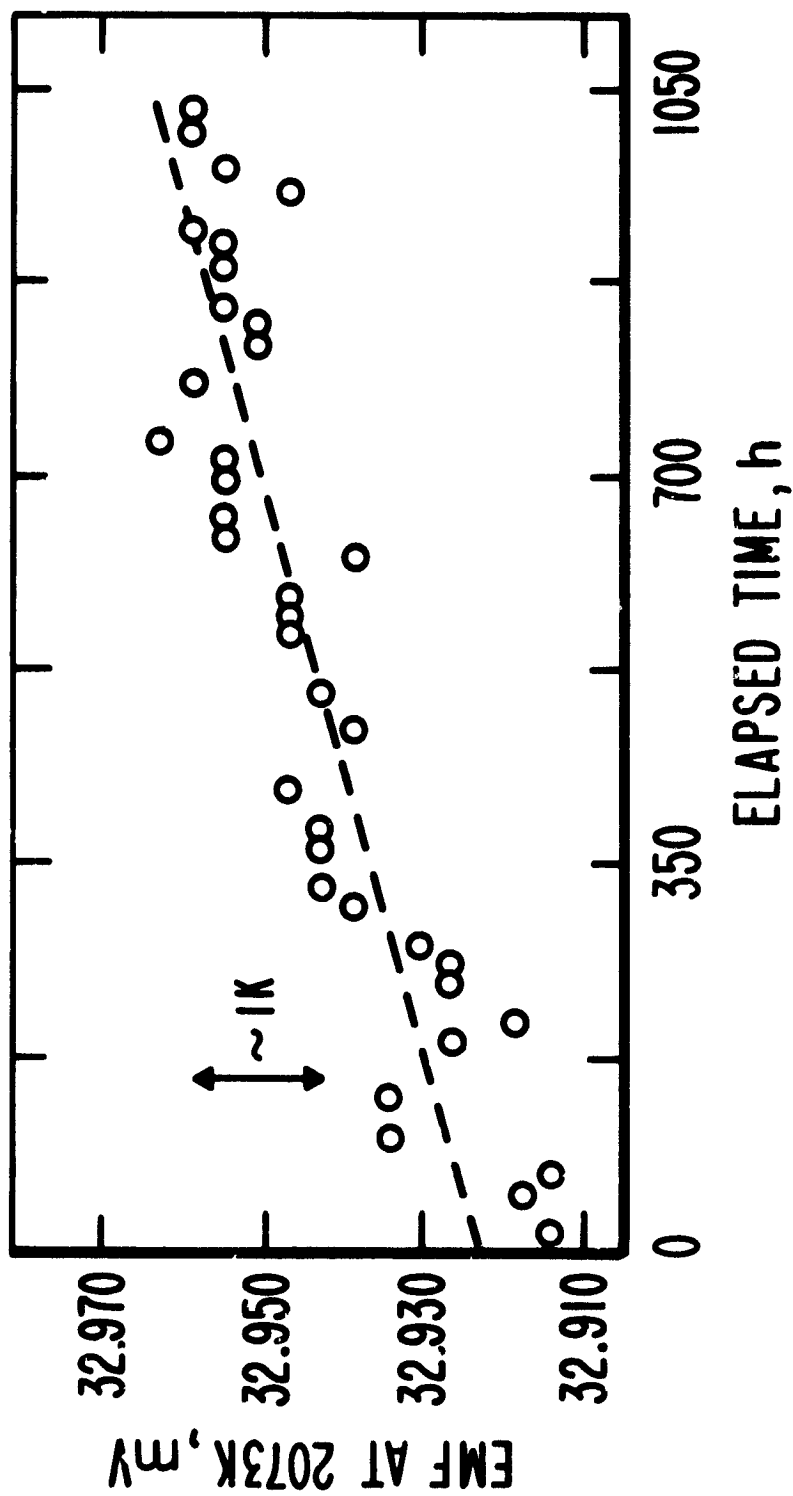


Figure 19. Drift in the thermal emf of a BeO-insulated W-3% Re versus W-25% Re thermocouple exposed at 2073 K in argon and in the presence of tantalum for 1029 hours. The curve through the data points is a straight line fit to the data by the method of least squares. The thermocouple was heated in the high temperature furnace and the temperature was measured with an automatic photoelectric optical pyrometer.

TABLE VI. SUMMARY OF THE RESULTS OF THE 1029 HOUR DRIFT TEST AT 2073 K IN ARGON  
WITH BeO-INSULATED W-3% Re VERSUS W-25% Re THERMOCOUPLES

RESULTS EXPRESSED IN TEMPERATURE EQUIVALENTS

Thermocouple No.	Automatic Photoelectric Optical Pyrometer as Reference <sup>a</sup>				Visual Optical Pyrometer as Reference				Approximate Relative Position of Thermocouple Measuring Junction in the Ta Blackbody Enclo- sure		
	Observer No. 1 <sup>a</sup>				Observer No. 2 <sup>b</sup>						
	S mK/h	$\sigma_s$ mK/h	$\sigma_r$ K		S mK/h	$\sigma_s$ mK/h	$\sigma_r$ K				
1	+2.9	0.2	0.4		+3.1	0.3	0.6	+2.8	0.7	1.2	center
2	+2.5	0.2	0.4		+2.6	0.3	0.6	+2.4	0.7	1.1	2.5 cm above center
3	+2.3	0.2	0.4		+2.4	0.3	0.6	+2.4	0.8	1.2	2.5 cm below center

S = slope of straight line fit to drift data by method of least squares.

$\sigma_s$  = standard deviation of slope.

$\sigma_r$  = standard deviation of residuals.

<sup>a</sup> 37 data points.

<sup>b</sup> 34 data points.

$\leq 1.5$  K for the visual pyrometer). The spectral transmittance of the furnace window was checked before and after the test and no significant change was detected in it ( $\leq$  equivalent of 1 K). Systematic errors introduced by other means, such as a drift in the calibration of the emf measuring equipment or a gradual change in blackbody conditions, are thought to be small ( $\leq$  equivalent of 0.3 K). Variations in the temperature of the thermocouple reference junctions and residual emfs in the measuring circuitry are negligible factors.

The question remains then as to whether the observed changes are due to a change in the thermocouples or whether they reflect changes in the measuring instruments and experimental apparatus. If the above allowances for systematic error are added, one gets 1.8 K for the measurements with the automatic photoelectric optical pyrometer. The observed changes in the thermocouples after testing for 1029 hours are slightly larger than this (see Table VI). We therefore conclude that at least part of the observed changes result from an actual drift in the thermocouples.

This experiment demonstrates that BeO-insulated W-Re thermocouples can be exposed to high temperatures (2073 K) in the presence of tantalum, and that such a combination can result in highly reliable performance for extended periods. This result is possible if high purity BeO is used, if the BeO is carefully degassed prior to use, if the thermoelements are properly aged, and if a high purity argon environment is maintained. It can be noted that others have surmised that reasonable results might be expected with this particular combination of materials if extreme care is employed and if the BeO insulator is of high purity (ref. 12).

#### CONCLUDING REMARKS

This report has presented studies of the effects of high temperature exposure of bare-wire W-Re alloy thermoelements and BeO-insulated W-3% Re and W-25% Re thermoelements in various high purity gaseous environments. The principal results obtained are as follows:

##### I. Bare thermoelements of 0.25 mm diameter.

###### A. Shift.

###### 1. Studies with the W-3% Re thermoelement.

Aging studies to determine the time-temperature parameters of the shift in the emf-temperature relationship of the W-3% Re thermoelement were performed with special wire that was obtained directly from a wire manufacturer (not a thermocouple wire supplier). This wire had not been given a prior stress-relief anneal. Therefore, the shift was large (equivalent  $\Delta T$  about + 55 K at 2073 K for aging in argon). With exposure in argon about 90% of the shift occurred after 2 minutes at 2400 K or after 1 hour at 2000 K; thermal aging was essentially complete after 1 hour at 2400 K. Since thermoelements obtained from commercial thermocouple wire suppliers have normally been given some heat treatment by the supplier, the shift would then be smaller. The shift for seven different lots of commercial W-3% Re thermocouple wire examined in this and a previous study ranges from about 10% to 40% of that given above. Thermal aging for these lots was also essentially complete after 1 hour at 2400 K in argon.

A small but significant difference in the shift was noted between aging in argon and aging in hydrogen. For each of three different lots of wire, the shift in argon minus the shift in hydrogen was equivalent to  $6 \pm 2$  K at 2073 K.

###### 2. Studies with the W-25% Re thermoelement.

Aging studies to determine the time-temperature parameters of the shift in the emf-temperature relationship of the W-25% Re thermoelement were performed with a lot of wire that had been given a short anneal at about 1200 K by the manufacturer after drawing. The shift in this lot of wire was small (equivalent  $\Delta T$  about +10 K

at 2073 K). The shift was essentially complete after aging in argon or in hydrogen for 1 hour at 2000 K or for a few minutes at 2400 K. For seven different lots of commercial W-25% Re thermocouple wire that have been tested the shift has also been small ( $< 10$  K at 2073 K in all cases).

The shift is the same in all ~~environments~~ <sup>environments</sup> (A, H<sub>2</sub>, He or N<sub>2</sub>). The thermoelectric properties of the thermoelement are virtually the same after aging for 1 hour in high purity argon at any temperature in the range 2000 to 3000 K.

3. Studies with other W-Re alloy thermoelements ("doped" W, "doped" W-5% Re, and "undoped" W-5% Re).

Studies of the shift (and of the drift) of other W-Re alloy thermoelements were performed with wire obtained from commercial thermocouple wire suppliers. For the lots tested, the shift after exposure in argon at 2400 K was large, ranging from about + 400 to + 500  $\mu$ V at 2073 K (equivalent  $\Delta T$  of about + 22 K to + 36 K, depending upon the thermocouple type). About 60% of the shift occurs during the first hour of exposure at 2400 K; the shift is essentially complete within 50 hours of exposure.

#### B. Drift.

1. Studies with W-3% Re and W-25% Re thermoelements.

These tests were performed with thermoelements obtained from commercial thermocouple wire suppliers. Tests were performed exposing the thermoelements at 2400 K in high purity nitrogen gas and helium gas environments, to complement previous studies in argon and hydrogen gases. The thermoelements exhibited no significant change (drift) in their emf-temperature relationship for time periods up to 500 hours, after the initial shift was completed.

2. Studies with other W-Re alloy thermoelements ("doped" W, "doped" W-5% Re, and "undoped" W-5% Re).

With exposure at 2400 K in argon for time periods up to 500 hours, no significant drift in the emf-temperature relationship was detected after the initial shift was completed.

#### C. Grain structure and ductility.

1. W-3% Re thermoelements.

Aging of the "doped" W-3% Re thermoelement in argon for 1 hour at any temperature up to about 2600 K results in only a slight modification in its microstructure, in that the fibrous or a small-grained structure is retained (only primary recrystallization occurs). Thermoelements of 0.25 mm diameter aged in this manner exhibit excellent room temperature bend ductility, and coiling around a mandrel four times their diameter is usually possible. Thermal aging at about 2700 K or above results in the formation of very large interlocking elongated grains (secondary recrystallization), accompanied by a marked decrease in room temperature ductility. While the microstructure and the mechanical properties of the W-3% Re thermoelement are dependent upon the aging temperature, the thermoelectric properties of the thermoelement are virtually the same after aging for 1 hour in high purity argon at any temperature in the range 2300 to 3000 K.

2. W-25% Re thermoelements.

The W-25% Re thermoelement is not a "chemically doped" alloy and upon aging in argon at temperatures of about 1800 K or above equiaxed grains are formed. The grain size is strongly dependent upon the time and temperature of aging, and the pliability of the thermoelement at room temperature decreases as the grain size increases. Therefore, time-temperature parameters must be carefully

controlled during aging so as to minimize grain growth. Aging for 1 hour at 2000 K or for a few minutes at 2400 K leaves the thermoelement fully recrystallized with only a moderate amount of grain growth, and it is ductile enough to be repeatedly coiled around a 20 mm diameter mandrel. In applications where extreme pliability is essential, aging of the W-25% Re thermoelement for only a few minutes at 1900 to 2000 K is recommended. This may leave a small amount of residual emf shift, but the thermoelement remains very pliable.

3. Other W-Re alloy thermoelements ("doped" W, "doped" W-5% Re and "undoped" W-5% Re).

In the "doped" W and "doped" W-5% Re thermoelements, a large, interlocking, elongated grain structure (secondary recrystallization) was exhibited after exposure at 2400 K in argon for extended periods (in excess of 50 hours). The formation of the larger grain structure resulted in a marked decrease in the room temperature bend ductility of the W thermoelement; the "doped" W-5% Re thermoelement remained ductile in that it could be coiled around a 1 mm diameter mandrel.

The "undoped" W-5% Re thermoelement exhibited an equiaxed grain structure after the initial high temperature exposure, and it had essentially no room temperature bend ductility. After 500 hours of exposure at 2400 K, the average grain size (typically 30  $\mu\text{m}$ ) was considerably smaller than in the W-25% Re thermoelement, which typically exhibited grain sizes of the order of 100  $\mu\text{m}$  after a similar exposure.

II. Studies with BeO-insulated thermoelement and thermocouple assemblies.

A. Exposure of BeO-insulated thermoelements to high temperature by electrically heating the thermoelements.

Exposure of the BeO-insulated thermoelements in argon at 2000 K by electrically heating the thermoelement resulted in the preferential loss of W from the W-Re alloys, presumably as a volatile oxide, and the subsequent deposit of W as a coating upon the bore of the BeO tubing. For the W-3% Re thermoelement, a decrease in diameter of as much as 10% occurred with exposure for 50 hours. For the W-25% Re thermoelement, a porous surface layer (up to 35  $\mu\text{m}$  in depth) occurred, and the grains in the surface layer were Re enriched to as much as W-45% Re; no appreciable change in the diameter of the thermoelement was exhibited. Prolonged high temperature vacuum degassing of the BeO tubing prior to exposure of the insulated thermoelements reduced, but did not eliminate, the preferential loss of W. The behavior observed is thought to be hastened by the radial temperature gradient that exists at the BeO-thermoelement interface due to manner of heating. The gross physical and chemical changes at the surface of the thermoelements resulted in only relatively small changes in their emf-temperature relationship. Chemical contamination of the thermoelements by metallic impurities transferred from the BeO tubing was not a serious factor.

B. Exposure of BeO-insulated thermoelement and thermocouple assemblies by heating in a furnace.

1. Thermoelement-BeO compatibility.

BeO-insulated W-3% Re and W-25% Re thermoelements exposed in the high temperature furnace in argon at 2000 and 2073 K for periods from 50 up to 1029 hours exhibited no evidence of preferential loss of tungsten. Serious incompatibility problems were encountered only when the BeO tubing was not properly degassed prior to use; adhesion of the thermoelement to BeO tubing at points within the bore then occurred. Chemical contamination of the thermoelements by metallic impurities transferred from the BeO tubing or surroundings was not a serious problem.

## 2. Physical and chemical changes in the BeO.

The BeO grain size (1 to 5  $\mu\text{m}$  in the "as received" material) was virtually unchanged after vacuum degassing at temperatures up to 1800 K and after exposure at 2000 K in argon for 50 hours. Exposure of the BeO tubing in argon while in the presence of Ta at nominally 2070 K resulted in substantial grain growth; grain size was then typically 30 to 60  $\mu\text{m}$  after 1029 hours of exposure and the BeO tubing acquired a translucent appearance.

A significant reduction of the detectable metallic impurities in sintered BeO tubing occurs with degassing and with exposure in argon at 2073 K in the presence of Ta. The total detectable impurities were reduced from 769 ppmw for the "as received" BeO tubing to 69 ppmw for the BeO tubing that was exposed in argon for 1029 hours at 2073 K while in the presence of Ta. Degassing in high vacuum at temperatures to 1800 K resulted in a large reduction in the impurity level of Si but little change in the impurity levels of Al, Ca and Mg.

## 3. Thermocouple drift test.

Three BeO-insulated W-3% Re vs W-25% Re thermocouples were formed using aged thermoelements and degassed high purity sintered BeO tubing. Exposure of the thermocouples in argon and in the presence of Ta (a Ta blackbody enclosure) at 2073 K resulted in only a small positive drift in their thermal emfs, equivalent to about 2 to 3 % during 1029 hours of test. The drift in the thermal emf of all three thermocouples at 2073 K was roughly linear with respect to time.

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